



Determination of carbonate vein chemistry using portable X-ray fluorescence and its application to mineral exploration

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Abstract: The composition of carbonate minerals infilling hydrothermal veins can vary as a function of factors including fluid chemistry, temperature and pressure. If effectively quantified, carbonate vein chemistry can represent an important tool in mineral exploration. We present a method for determining carbonate vein chemistry using portable X-ray fluorescence analysis (pXRF) utilising matrix matched certified reference materials (CRMs) to assess pXRF analyser performance, before establishing strict QA/QC procedures, along with linear calibration equations for Mg, S, Mn, Fe, Zn, Sr and Pb. However, low concentrations of mineralization-related elements in commercially available CRMs meant raw S, Zn and Pb concentrations determined for case study samples could not be reliably corrected. Our new workflow was then applied to carbonate vein samples collected from Mount Isa, Northwest Queensland, Australia. Though complexity of this system limited the interpretation of results, the case study showed that pXRF can also be used to identify veins with multiple generations of carbonate infill. Portable X-ray fluorescence analyses, used in conjunction with robust QA/QC processes is a powerful tool that can quickly and cost-effectively inform decisions during exploration programs.

Keywords: portable XRF; carbonate vein; Mount Isa; exploration targeting

Supplementary material: Results of pXRF analyser performance for six reference materials (S1) and results from analysis of carbonate veins collected from Mount Isa, Australia (S2). All tables are available at <https://doi.org/10.6084/m9.figshare.c.3831385>

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Carbonate minerals are ubiquitous vein-infilling materials associated with many styles of hydrothermal mineralization, including skarn, Carlin-type gold, mesothermal gold, porphyry, low-sulphidation epithermal gold and Mount Isa-type sediment hosted Cu deposits. Commonly considered gangue minerals of little or no significance, understanding how the composition of carbonate minerals can vary as a function of fluid chemistry, temperature and pressure means that carbonate minerals could be an important tool in mineral exploration. Recognition that the composition of calcite veins differed around ore deposits dates back to at least the late 1950s, with Stone (1959) recognizing that the very well-known Naica carbonate replacement deposit in Mexico contained fluorescent calcite in the regions adjacent to Pb–Zn–Ag mineralization, whereas distal marbles did not fluoresce. Modern, handheld analytical technology such as portable X-ray fluorescence (pXRF) allows direct and quantitative chemical measurements to be made in the field. These can be used to support UV fluorescence observations, which are common mineral industry practise. Here we present a method for quantifying carbonate vein chemistry using pXRF analysis, which can be quickly and cost-effectively employed during mineral exploration.

Carbonates are a group of minerals in which the $(\text{CO}_3)^{2-}$ ion is the essential unit (Chang *et al.* 1998). They can be divided into two structural groups, rhombohedral carbonates, (which can be subdivided into calcite and dolomite groups), and orthorhombic carbonates. Common rock forming minerals in the calcite group are calcite (CaCO_3), magnesite (MgCO_3), siderite (FeCO_3) and rhodochrosite (MnCO_3), while dolomite ($\text{CaMg}(\text{CO}_3)_2$), ankerite ($\text{CaFe}(\text{CO}_3)_2$)³ and kutnohorite ($\text{CaMn}(\text{CO}_3)_2$) are contained in the dolomite group. Typically, other elements will substitute for cations when carbonate minerals precipitate from solution. The concentration of minor-to-trace elements within carbonate minerals will reflect a variety of factors in the fluid from which carbonate

precipitated. The major factors controlling trace element partitioning between crystal and liquid are the size of the cation site, and the ionic radius of the substituting element. In calcite, the Ca site will typically be filled with various cations of Mn^{2+} , Fe^{2+} , Mg^{2+} and to a lesser extent Sr^{2+} , Ba^{2+} and Pb^{2+} . While in dolomite, the Mg site will typically be filled with Fe^{2+} and Mn^{2+} (Chang *et al.* 1998).

A number of physiochemical factors will also affect the concentration of trace elements in carbonates, including the concentration of the substituting elements in the solution, the rate of precipitation, temperature, Eh, pH, f_{CO_2} and salinity (Simmons *et al.* 2000). Numerous studies have addressed the incorporation of Mg^{2+} and Sr^{2+} into calcite and found a strong relationship between temperature, precipitation rates and incorporation of these cations (Mucci & Morse 1983; Wasylenki *et al.* 2005, and references therein). In general, high precipitation rates lead to the higher concentrations of both Sr and Mg, while lower precipitation rates and higher temperatures result the incorporation of more Fe^{2+} and Mn^{2+} (Mucci & Morse 1983). Fluid composition is also critical, which will control what trace elements are transported in the crystallizing fluid, and will also control how these trace elements are incorporated during carbonate precipitation. For example, the presence of Mn and Mg in fluid will result in coupled substitution of Sr into the calcite crystal lattice (Ichikuni 1973; Carpenter & Lohmann 1992). Hence, variations in trace element concentration in carbonate can be used to make inferences about temperature variation and precipitation rates during vein growth. However, these interpretations are only valid if the fluid composition remains constant. Conversely, in systems where evidence suggests temperature remained approximately constant during vein formation, changes in trace element composition of the vein could be interpreted in terms of changing fluid composition.

The chemistry of low temperature carbonates ($<200^\circ\text{C}$) is well documented and underpins reconstructions of ocean temperature

(Barker *et al.* 2005, and references therein) and the understanding of diagenetic processes that affect petroleum reservoir characteristics (e.g. Hood *et al.* 2004). Alternatively, the chemistry of high temperature carbonates associated with hydrothermal systems is considered less often and little experimental data is available to aid interpretation of the composition of hydrothermal carbonate minerals (e.g. Pearce *et al.* 2013). However, changes in the composition of carbonate minerals around hydrothermal ore deposits have various potential uses, including establishment of paragenetic sequences within ore deposits, identifying cryptic alteration distal to mineralization, and aiding exploration activities. At the El Peñón low sulphidation epithermal Au-Ag deposit, Chile, paragenetically early calcite veins associated with precious metal mineralization are compositionally complex (Bissig *et al.* 2010). This generation of veins contains high concentrations of Fe, Mn, Mg, Pb and Zn when compared with late stage calcite veins. This difference in carbonate chemistry is attributed to changes in temperature, with late stage calcite veins probably forming from cooler, steam-heated fluids in the waning stages of the hydrothermal system. Vaughan *et al.* (2016) used calcite chemistry linked to carbon and oxygen stable isotope compositions to understand carbonate veins of unknown affinity at the Banshee Carlin-type Au deposit on the northern Carlin trend, Nevada. In that study, elevated Mn concentrations, anomalous Eu contents and coincident depletion of $\delta^{18}\text{O}$ in intermediate stage calcite veins were identified as being temporally coincident with alteration associated with Au mineralization. It was suggested that the recognition of syn-alteration veins could be used to identify the distal margins of low-temperature hydrothermal mineralization at Banshee and potentially other Carlin-type gold deposits (Vaughan *et al.* 2016).

Though pXRF has been used to determine the chemistry of carbonate lithologies (Quye-Sawyer *et al.* 2015), it has not been employed to quantify the composition of carbonate veins associated with hydrothermal systems. Historically, the composition of carbonate veins has been determined by a range of quantitative and qualitative methods. Quantitative methods for determining carbonate composition include wet-chemical analysis, X-ray diffraction (XRD), electron microprobe (EMP) analysis and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Wet-chemical analysis requires partial leaching using acid, such as 1 M HCL solution or acetic acid, which specifically targets carbonate minerals (Bissig *et al.* 2010). This solution is then analysed using techniques such as ICP-MS. Determination of carbonate chemistry by XRD can be utilized by measuring a *d*-value or cell parameter sensitive to composition. As these two methods require vein samples to be presented as powder, they can be considered bulk analytical methods (Essene 1983). Conversely, EMP and LA-ICP-MS analysis are carried out on polished sample blocks and can be considered as non- to micro-destructive analytical techniques. The high spatial resolution of both techniques means individual grains can be analysed *in situ*, allowing investigation of chemical relationships between grains (Reed 2005). Though all these methods can produce accurate and precise analysis, they can be costly and time consuming, are limited to the laboratory environment, and are generally only employed as part of characterization studies.

Ultraviolet light is commonly used in mineral exploration as a qualitative method for determining carbonate chemistry. Calcites show fluorescence at various wavelengths as a result of elevated levels of activator elements including Mn with Pb as a sensitizer, REEs, and Zn, or fluorescence due to lattice defects (Schulman *et al.* 1947; Gies 1975). Additional impurities such as Sn, Mg, Bi, La and Nd result in a wide range of fluorescence colours varying from pale blue to red, yellow and green. Dolomite is not a strongly luminescing carbonate, though pale-blue luminescence has been reported (Przibram 1956). Elevated levels of Fe, and to a lesser

extent Mg and Ni, in the crystal lattice will quench luminescence (Gies 1975). Therefore, while the UV fluorescence technique is cheaply and easily employed in the field, it remains less effective in environments where carbonates such as siderite, ankerite, ferroan dolomite and magnesite are common.

Continued expansion in availability and use of portable X-ray fluorescence analysers in mineral exploration provide an alternative method for determining vein carbonate chemistry. The portability and speed with which analyses can be obtained makes the technique suitable for informing decisions in the field during exploration programs. In this study we investigate the use of pXRF to determine carbonate chemistry of veins associated with hydrothermal systems and present an application of data obtained using a pXRF analyser.

Case study

This study presents results from pXRF analysis of samples from two base metal deposits at Mount Isa, Northwest Queensland, Australia (Fig. 1). Samples were collected in diamond drill holes at varying distances from ore bodies at Mount Isa Mine and George Fisher Mine, as part of a wider study to identify cryptic alteration associated with Cu mineralization.

Carbonates are a ubiquitous feature of base metal deposits at Mount Isa. Chapman (1999) established a comprehensive paragenetic sequence characterizing all carbonate phases, including primary sedimentary carbonate in the Urquhart Shale, carbonate associated with diagenetic and hydrothermal alteration, and vein carbonate. Vein carbonates can be further divided into three separate syn-diagenetic veins; sugary Fe dolomite veins which formed post sphalerite mineralization and syn- to late-tectonic veins associated with Cu mineralization (Chapman 1999). Mineralogy of all generations of carbonate at Mount Isa is dominated by calcite, ferroan dolomite and to a lesser extent ankerite and siderite (e.g. Valenta 1988; Waring 1990; Chapman 1999). This study focuses on the chemistry of vein carbonates.

Mount Isa Mine is a world class base metal deposit containing pre-mining resources of 255 Mt at 3.3 Cu and 150 Mt at c. 6% Pb, c. 7% Zn and 160 g/t Ag in spatially associated yet separate orebodies (Williams 1998). Pb-Zn-Ag orebodies consist of steeply dipping strata-bound lenses organized in an *en echelon* pattern that interdigitates with Cu orebodies down-dip towards the south. Copper orebodies comprise syn- to late-tectonic vein- or breccia-hosted mineralization, which sits within a zoned alteration envelope, known as the silica-dolomite (Perkins 1984). The core of this alteration halo is dominated by highly silicified, brecciated shale and chalcopryite and/or quartz matrix breccias. Dolomite in the alteration envelope increases in abundance away from the basement contact with the underlying Eastern Creek Volcanics of the Haslingden Group.

George Fisher mine is situated 25 km north of the Mount Isa deposit. Both deposits are hosted by the Urquhart Shale of the Mount Isa Group. George Fisher contains 108 Mt at 5.4% Pb, 11% Zn and 93 g/t Ag in stacked, strata-bound lenses in similar style to Mount Isa (Chapman 2004). The striking difference between the two deposits is the paucity of syn- to late-tectonic Cu mineralization and associated silica dolomite alteration at George Fisher (Chapman 2004). This difference between the two deposits provides the opportunity to examine the nature of carbonates in the absence of extensive Cu mineralization.

Materials and methods

Instrument, settings and materials

The instrument used for this study is the Olympus DELTA Premium XRF analyser, with a 4 W (40 kV) Rh X-ray tube and large-area

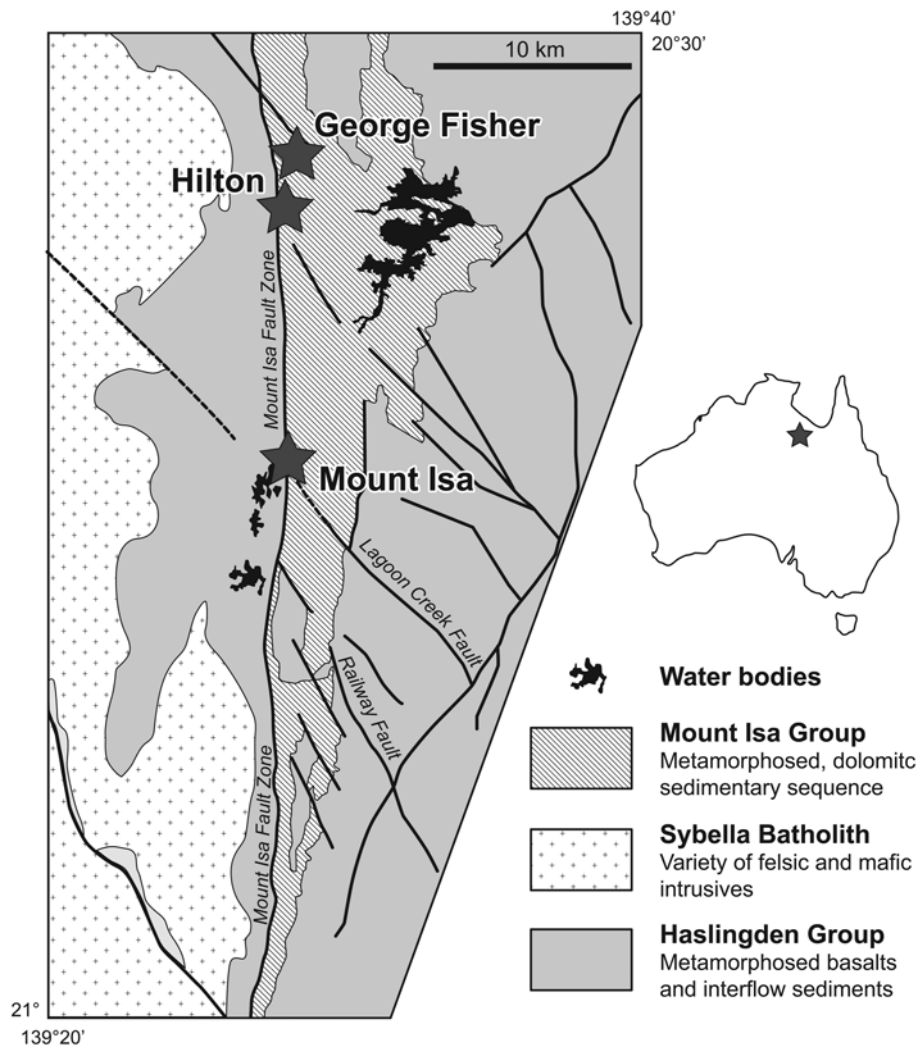


Fig. 1. Simplified geology of the area around Mount Isa, showing the distribution of the three main Proterozoic units (after *Wilde et al. 2006*).

silicon drift detector. This portable XRF offers two different analytical modes, the 3-beam (at 40, 40 and 15 kV) 'soil' mode and 2-beam (at 40 and 10 kV) 'geochem' mode. Beam count times can be varied independently between 10 and 60 seconds, resulting in total run times between 30 and 180 seconds. For the purpose of this study, samples were analysed using geochem mode, with beam count times set at 30 seconds for both the 40 and 10 kV beams (*Fisher et al. 2014*). The unit was used in an uncollimated configuration during this study, with a beam width of 8–10 mm. As such, veins less than 8 mm in width could not be analysed. All samples were analysed in a portable workstation.

Samples used during this study consisted of hand specimens of sawn quarter-core. Though *Gazley & Fisher (2014)* showed that variation in elemental concentrations is greatly reduced when analysis is carried out on crushed and pulverized core, this is not applicable in the study given the nature of samples to be analysed. Given this, all analyses were carried out directly on the flat surface of freshly cut core, rather than the curved surface, to minimize variability in element concentration (*Fisher et al. 2014; Gazley & Fisher 2014*). We chose to analyse unpolished surfaces in this study as precision is affected to a greater extent by grain size and sample heterogeneity than small scale surface morphology (*Morris 2009; Gazley & Fisher 2014; Le Vaillant et al. 2014; Ross et al. 2014*).

Standards used in the study consisted of five commercially available matrix-matched certified reference materials (CRMs) and four reference materials (RMs) created as part of this study (Supplementary material, table 1). RMs included one sample of analytical grade CaCO_3 and three samples consisting of mixtures of

a rhodochrosite concretion (BT5) collected from Cretaceous marine mudstones at Batley, New Zealand (*C.S. Nelson, pers. comm. 2017*), and a siderite concretion (TS5d) collected from Eocene coal measures at Rotowaro, New Zealand (*Pearson & Nelson 2005*). RMS were created to complement CRMs and fully cover the expected range of elemental concentrations from carbonate vein samples analysed.

Standards were prepared as pressed pellets as appropriate solid-rock standards were not available. Pressed powder pellets present a closer approximation of the density of samples analysed in this study than loose powder standards in sample cups, while also negating issues of heterogeneity related to grain size that arise with when using solid-rock standards (*Fisher et al. 2014; Gazley & Fisher 2014; Le Vaillant et al. 2014*). Their use as standards also negates the effects of contamination and attenuation by sample containers discussed by previous studies (e.g. *Gazley et al. 2011; Fisher et al. 2014; Gazley & Fisher 2014; Le Vaillant et al. 2014; Quye-Sawyer et al. 2015*).

Calibration

In this study, we generated linear calibration equations for elements most likely to substitute for major cations in the carbonate structure; Mg, Ca, Fe, Mn and Sr. Along with this, we also considered S, Zn and Pb, as they could be used to determine the possible presence of fine-grained sulphides.

To generate calibration equations, each standard was analysed 10 times using the pXRF analyser. For each of these elements listed

above, median values of the elemental concentration obtained by pXRF were plotted against certified values to calculate linear calibration equations. Where no certified values were available, as was the case with RMs, elemental concentrations were determined using a 1 KW Bruker S8 Tiger wavelength dispersive X-ray fluorescence (WDS-XRF) analyser at the University of Waikato, New Zealand. Major element concentrations were determined on fused glass disks cast using a 10:1 flux ratio, while trace element concentrations were determined using pressed pellets. Samples were analysed under vacuum, with trace element results calibrated against a series of international XRF reference materials using the values of Govindaraju (1994).

Precision, accuracy and detection limits

Determining precision, accuracy and detection limits are critical in assessing geochemical data (Jenner 1996). However, detection limits and, to a lesser extent, accuracy can be difficult to determine precisely for pXRF analysers (Gazley *et al.* 2011; Fisher *et al.* 2014; Gazley & Fisher 2014; Hall *et al.* 2014; Simandl *et al.* 2014).

In this study, we assessed both instrument and sample precision, following the studies of Le Vaillant *et al.* (2014) and Piercey & Devine (2014). Instrument precision was determined by completing 10 repeated analyses on exactly the same point for each pressed pellet CRM, while sample precision was determined by conducting multiple analyses on three samples from Mount Isa; EX096664 ($n = 15$), EX105617 ($n = 8$) and EX105636 ($n = 8$) (Fig. 2). Percentage relative standard deviation (RSD) was calculated for each element considered in this study, for each standard and sample, where the average value measured for the reference material was greater than the limit of quantification (LOQ) (Piercey & Devine 2014). Accuracy was determined by using percentage relative difference (RD) between the average elemental value determined by repeated measurements of CRMs and the certified value for a given element.

We report the limit of detection (LOD), defined as three times the standard deviation of replicate analysis on standards which contain relatively small amounts of various elements of interest (Le Vaillant *et al.* 2014). We also determined the limit of quantification, which is

calculated as being ten times the standard deviation (Keith *et al.* 1983; Jenner 1996). Between the LOD and the LOQ, results are in a region of less certain quantification. However, above the LOQ data may be treated quantitatively (Jenner 1996).

QA/QC and data management

Quality assurance and quality control (QA/QC) for pXRF analysis should be as robust as that required for conventional analytical methods if there is to be confidence in data generated. Calibration against CRMs and RMs can go some way to ensuring robust and comparable data-sets are generated over time. However, analyser performance also needs to be quantified. The performance of handheld pXRF analysers may be influenced by factors including the amount of time it has to warm up, and atmospheric conditions such as temperature and pressure (Fisher *et al.* 2014). Periodic replicate analyses of a SiO₂ blank and repeats of one CRM were used to monitor analytical drift and ensure the linear corrections applied to the samples were robust (Fisher *et al.* 2014; Gazley & Fisher 2014).

A relational database was established to record and archive results and QA/QC data, following the work flow established by Fisher *et al.* (2014), taking into consideration issues of data quality discussed by Gazley & Fisher (2014). Accepted results, consisting of calibrated, drift corrected and blank corrected analyses were appended into a data table. Meta-data, including details of the instrument used, analysis date, beam count times, nature of blank material used, and sample medium for each analysis were stored in a separate table linked to the data table by a unique identifier. In doing so, all data could be readily retrieved at any point after the analyses had been recorded.

Results

Precision, accuracy and detection limits

During this study, we evaluated both instrument and sample precision using certified reference materials and carbonate veins

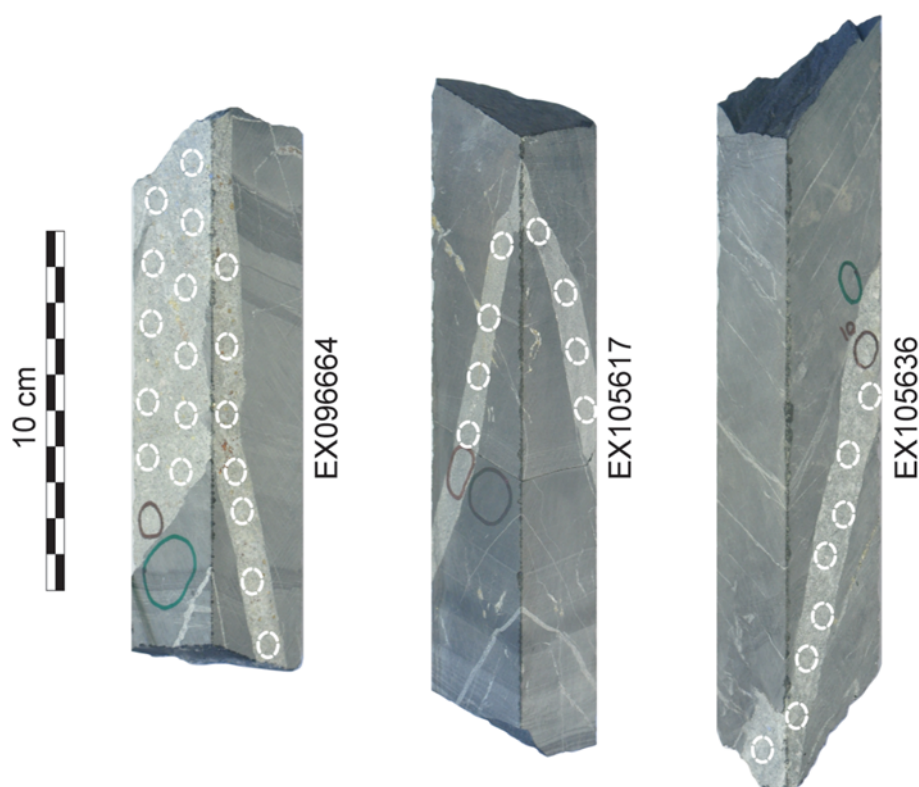


Fig. 2. Dolomitic shale-hosted vein carbonate samples from Mount Isa Mine, used to evaluate sample precision. White circles represent the location of pXRF analyses on the sample.

Table 1. Summary table of instrument precision

	x_{av}	σ	RSD	RD
Mg (%)	9.54–14.19	0.4–0.8	4.0–5.8	2.9–10.5
S (ppm)	216–2097	13.8–115.1	5.5–9.6	–79.1–25.3
Ca (%)	24.10–44.18	0.2–1.9	0.6–7.8	8.7–13.9
Mn (ppm)	168–909	15.3–19.6	1.7–9.4	5.1–31.8
Fe (ppm)	1971–5043	32.4–39.2	0.7–1.8	–1.2–4.2
Zn (ppm)	33–74	1.7–2.5	2.9–7.3	7.1–144.1
Sr (ppm)	26–477	0.5–4.2	0.6–2.1	4.1–3.5
Pb (ppm)	33	1.7	5.1	21.1

Ranges of average elemental concentration (x_{av}), standard deviation (σ), relative standard deviation (RSD) and percentage relative difference (RD) for CRMs where the average elemental concentration is greater than the limit of quantification.

samples respectively. Results show that instrument precision of the pXRF unit ranges from good to excellent based on the criteria of Jenner (1996), for the elements of interest in this study (Table 1, Supplementary material, table 1). This is as expected, as precision is concentration dependant (Jenner 1996) and the RSD was only considered for CRMs where the average elemental concentration of the standard was above the LOQ. Calcium and Sr have the lowest RSD values for an individual standard (RSD = 0.6%). Iron and Sr have the best overall precision with all RSD values within the range of excellent precision (RSD < 3%) for standards where the average elemental concentration is greater than the LOQ. Sulphur has the worst instrument precision of the elements considered in this study, with RSD values ranging between 5.5 and 9.6%. It is also important to note that though precision for Pb can be considered very good, only one of six CRMs had an average elemental concentration above the LOQ.

Sample precision obtained for carbonate veins from Mount Isa varies considerably (Table 2, Supplementary material, table 1). Precision for almost all elements considered for samples EX096664 and EX105617 can be considered to be poor (RSD > 10%) based on the classification of Jenner (1996). Conversely, for EX105636, sample precision for Mg, Ca, Fe and Mn range from very good to excellent. These results compare well to instrument precision determined for the pXRF analyser (Table 4). While sample precision determined for S, Zn and Pb for all samples is significantly worse than instrument precision.

While instrument precision ranges from good to excellent across all the elements considered in this study, accuracy of pXRF analysis for CRMs shows significantly more variability (Table 1, Supplementary material, table 1). Strontium and Fe show the greatest accuracy, with the maximum percentage relative difference being roughly $\pm 4\%$. Other major elements, including Mn and to a lesser extent Mg and Ca, have greater variability in accuracy. Sulphur shows the greatest variability in accuracy. Even as the average elemental concentration approaches $10\times$ the LOD, the

percentage relative difference is still -46.6% . This emphasizes that to obtain accurate data either a preloaded instrument carbonate calibration or independent calibration using CRMs is required (as discussed below).

The LOD obtained for the elements of interest in this study varies ranging from 1.23% for Mg to 2 ppm for Sr (Table 3, Supplementary material, table 1). These compare well with previously reported limits of detection of different elements in various rock types by pXRF (e.g. Morris 2009; Le Vaillant *et al.* 2014).

Calibration Equations

Certified values plotted against values determined by pXRF for Mg, Ca, Fe and Sr demonstrate strong linear correlation, with correlation coefficients between 0.996 and 0.999, while correlation coefficients for S, Zn and Pb range from 0.905 to 0.958 (Fig. 3). However, calibration equations for S, Zn and Pb are problematic as many of the expected values of the CRMs sit at or below the limit of detection determined for the pXRF analyser, with the regression line propagated through a single sample. For this reason, S, Zn and Pb are not able to be reliably quantified for samples analysed from Mount Isa. However, poorly calibrated or raw results may still be used to qualitatively identify anomalous values, thereby highlighting analyses that may include sulphide minerals.

Discussion

Recommended Protocol

This investigation into the use of pXRF analysers in determining the chemistry of carbonate veins has allowed the development of a robust protocol which can be used to make decisions during mineral exploration programs in a time and cost effective manner. Drill core samples should be sawn in order to allow analysis on a flat surface (Morris 2009; Gazley & Fisher 2014; Le Vaillant *et al.* 2014). Geochem mode is preferred when using the Olympus DELTA Premium XRF analyser as it allows for the determination of Mg in samples, unlike soil mode.

Comparison of instrument and sample precision (Table 4) show that instrument precision outstrips sample precision as a result of heterogeneity in carbonate veins analysed in this study. For this reason, it is argued here that beam count times of 30 seconds for each beam provide the optimal mix of precision and sample through-put in this situation. However, if this not the case, ideal count times can be determined following the method of Fisher *et al.* (2014) or Ross *et al.* (2014).

Instrument performance will vary as a result of a number of environmental factors including temperature and pressure, along with other factors such as the amount of time the analyser has to warm up, age of the unit and time since last service (Fisher *et al.*

Table 2. Sample precision for elements considered in this study from three samples from Mount Isa Mine

	EX096664			EX105617			EX105636		
	x_{av}	σ	RSD	x_{av}	σ	RSD	x_{av}	σ	RSD
Mg (%)	8.66	1.1	12.3	9.20	1.3	13.9	8.67	0.6	6.7
S (ppm)	5737	3405	59.4	1481	1058	71.4	bd	–	–
Ca (%)	22.21	3.7	16.5	21.70	3.3	15.0	24.39	1.0	4.0
Mn (ppm)	2203	288	13.1	2661	176	6.6	2579	75	2.9
Fe (%)	4.40	0.8	17.5	3.89	0.4	9.2	3.28	0.2	5.9
Zn (ppm)	22	13	60.0	13	8	59.2	14	2	15.5
Sr (ppm)	53	5	10.2	49	29	59.4	82	12	14.4
Pb (ppm)	34	14	42.1	12	4	36.1	bd	–	–

bd, below detection.

Table 3. Summary table of detection limits determined for pXRF analysis

	x_{av}	σ	LOD	LOQ
Mg (%)	9.54 – 14.19	0.4 – 0.8	1.23	4.07
S (ppm)	216 – 2097	13.8 – 115.1	41	137
Ca (%)	24.10 – 44.18	0.2 – 1.9	0.55	1.82
Mn (ppm)	168 – 909	15.3 – 19.6	37	123
Fe (ppm)	1971 – 5043	32.4 – 39.2	97	321
Zn (ppm)	33 – 74	1.7 – 2.5	5	17
Sr (ppm)	26 – 477	0.5 – 4.2	2	5
Pb (ppm)	33	1.7	5	15

x_{av} and σ report ranges, while limit of detection (LOD) and limit of quantification (LOQ) results are median values for all CRMs where the average elemental concentration was greater than the LOQ of the standard.

Table 4. Comparison between instrument and sample precision

	Instrument RSD	EX096664 RSD	EX105617 RSD	EX105636 RSD
Mg	4.0 – 5.8	12.3	13.9	6.7
S	5.5 – 9.6	59.4	71.4	–
Ca	0.6 – 7.8	16.5	15.0	4.0
Mn	1.7 – 9.4	13.1	6.6	2.9
Fe	0.7 – 1.8	17.5	9.2	5.9
Zn	2.9 – 7.3	60.0	59.2	15.5
Sr	0.6 – 2.1	10.2	59.4	14.4
Pb	5.1	42.1	36.1	–

2014; Gazley & Fisher 2014). Therefore, robust QA/QC procedures are critical in maintaining data integrity. Selection of suitable CRMs is a critical aspect of QA/QC that allows the establishment of calibration equations and monitoring of instrument drift. However, sourcing commercially available CRMs that were matrix-matched with carbonate veins and covered the range of elemental concentrations observed during this study was difficult, particularly for trace elements. It is suggested that site specific RMs are established to help overcome this issue. In the case of this study, this was achieved by mixing known quantities of end member carbonates, siderite and rhodochrosite. Alternatively, project specific samples with a range of elemental concentrations could be analysed using standard analytical techniques such as XRF or ICP-MS to determine expected values (e.g. Le Vaillant *et al.* 2014). Splits of these samples could then be analysed by pXRF to define linear calibration equations. Similar problems were faced with elements associated with sulphide minerals (i.e. S, Zn and Pb). Thus, if this technique is to be adopted by industry, we recommend establishment of commercial CRMs from carbonate-hosted mineral deposits to enable easy calibration of mineralization-related elements.

Case study

The paragenetic sequence recorded in carbonate veins at Mount Isa is complex, reflecting at least three stages of vein formation over a protracted period following deposition of the Urquhart Shale at Mount Isa (1652 ± 7 Ma; Page & Sweet 1998) through to Cu mineralization (c. 1523 Ma; Perkins *et al.* 1999). The hydrothermal system responsible for Cu mineralization and development of the silica-dolomite alteration halo resulted in pseudomorphic replacement of earlier carbonate phases through dissolution and recrystallization processes (Perkins 1984; Swager 1985; Waring 1990; Chapman 1999). During this period, there is evidence of multiple phases of brecciation (Taylor 2010) and the precipitation of three different types of dolomite veins, some of which contain calcite inclusions (Waring 1990). Visual differentiation of these carbonate species is almost impossible, but can be aided by carbonate staining using Alizarin red S in HCL (Waring 1990; Chapman 1999).

Given this complexity, EMP analysis shows that vein carbonates fit within one of three groups: (1) dolomite-ankerite solid solution; (2) magnesite-siderite solid solution; and (3) a near-pure-calcite end member (Valenta 1988; Waring 1990; Chapman 1999). When plotted on a $\text{CaCO}_3\text{-MgCO}_3\text{-Fe + MnCO}_3$ ternary plot, these groups fall along tightly constrained trends (Fig. 4), even though each group contains multiple stages of veining. In contrast to this, carbonate vein chemistry determined by micro-drilling and wet-chemical methods as part of previous studies (e.g. Hannan 1991; (C.L. Waring, pers. comm., 1991)) and ongoing geochemical exploration by MIM show a great deal of variation. Though many results sit within the compositional fields established by EMP studies, a number of samples fall along a mixing trend between calcite and ferroan dolomite. This variation in carbonate chemistry for samples analysed by wet-chemical methods is attributed to bulk nature of the method. This is supported by XRD studies of powders prior to acid-digestion, which show vein samples obtained by micro-drill or hand picking commonly consist of multiple species of carbonate (Hannan 1991).

Results obtained by pXRF analysis show similar patterns of variation in carbonate chemistry for samples collected from both Mount Isa Mine and George Fisher (Fig. 4). As with results determined by wet-chemical methods, vein analyses that plot outside the defined compositional fields are interpreted to contain carbonates from multiple groups. Heterogeneity in carbonates veins due to paragenetic complexity of the Mount Isa system is effectively averaged across the area of the pXRF measurement window (c. 1.5 cm^2 for the uncollimated beam used). For this reason, it is suggested that in this application, pXRF analysis represents a ‘bulk’ analytical technique, similar to wet-chemical methods or XRD. Further to this, this technique could accurately replace these methods in a mineral exploration field setting.

Though paragenetic complexity limits the extent to which these data can be used to assess spatial variation of carbonate vein chemistry at Mount Isa, the bulk nature of this approach could be used to assess complexity and indicate the presence of multiple generations of carbonate infill in other systems. Where paragenetic sequences have been established and vein carbonate phases characterized by EMP or LA-ICP-MS, the presence of multiple generations of carbonate infill could be determined by plotting

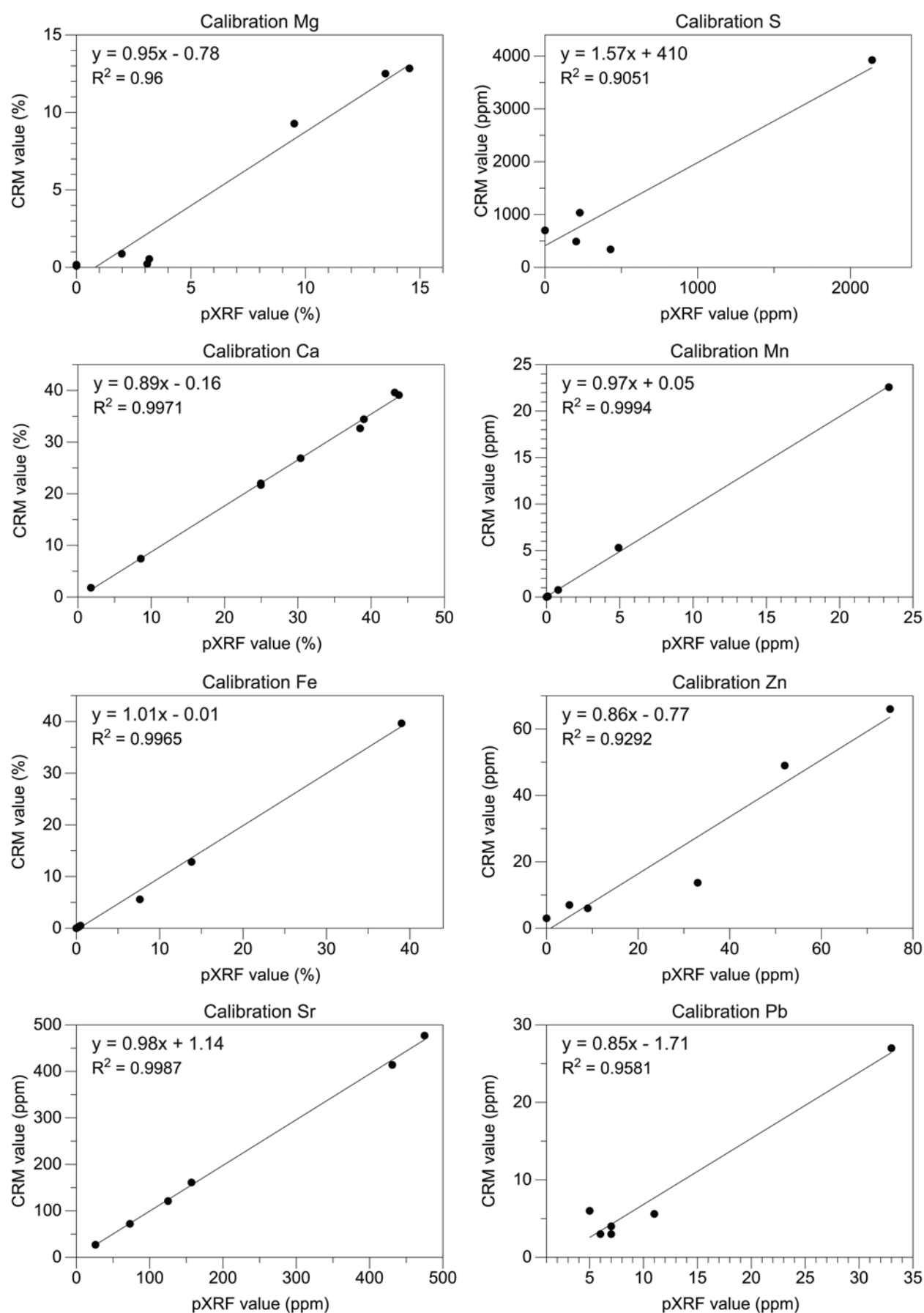


Fig. 3. Calibration curves for Mg, S, Ca, Mn, Fe, Zn, Sr and Pb. Calibration curves are analyser specific and can only applied to matrix-matched samples.

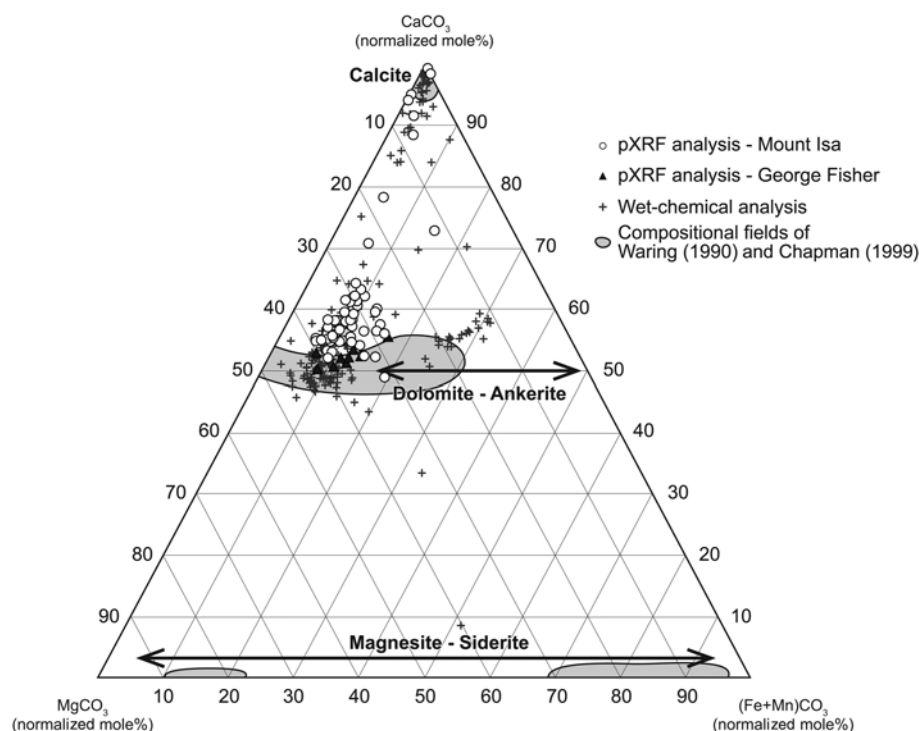


Fig. 4. Ternary diagram showing chemistry of carbonate vein samples from Mount Isa Mine and George Fisher Mine determined by pXRF, wet-chemical analysis (results provided by Mount Isa Mines Resource Development) and vein carbonate compositional fields determined by electron microprobe analysis (Waring 1990; Chapman 1999).

results on a ternary diagram similar to Figure 4. As at Mount Isa, analyses falling on mixing trends between defined groups will represent veins with multiple generations of infill. In systems where carbonate mineral groups have not been characterized, multiple analyses of individual veins could be used to assess complexity. When plotted on a ternary plot of CaCO_3 - MgCO_3 - $\text{Fe} + \text{MnCO}_3$, veins with a single generation of carbonate infill show little variation in carbonate composition, as shown by EX105586a and EX105586b which also plot within the defined compositional fields for Mount Isa (Fig. 5). However, samples with multiple generations of carbonate infill exhibit much greater variation, shown by samples selected from the calcite-ferroan dolomite mixing trend in Figure 4. This variation will be site specific, however once identified, could warrant further characterization of the system.

Conclusion

The results from this study show that pXRF, coupled with robust QA/QC procedures can be used to accurately determine the chemistry of carbonate veins associated with hydrothermal systems. Matrixed-matched reference materials were successfully used to develop linear calibration equations for carbonate related elements. However, currently available CRMs are in adequate for development of calibration equations for mineralization-related elements. For this reason, we recommend the development of commercially available CRMs with elements in a carbonate matrix.

The results obtained by pXRF on carbonate vein samples from Mount Isa and George Fisher base metal deposits compare well with results previously determined by wet-chemical methods. However,

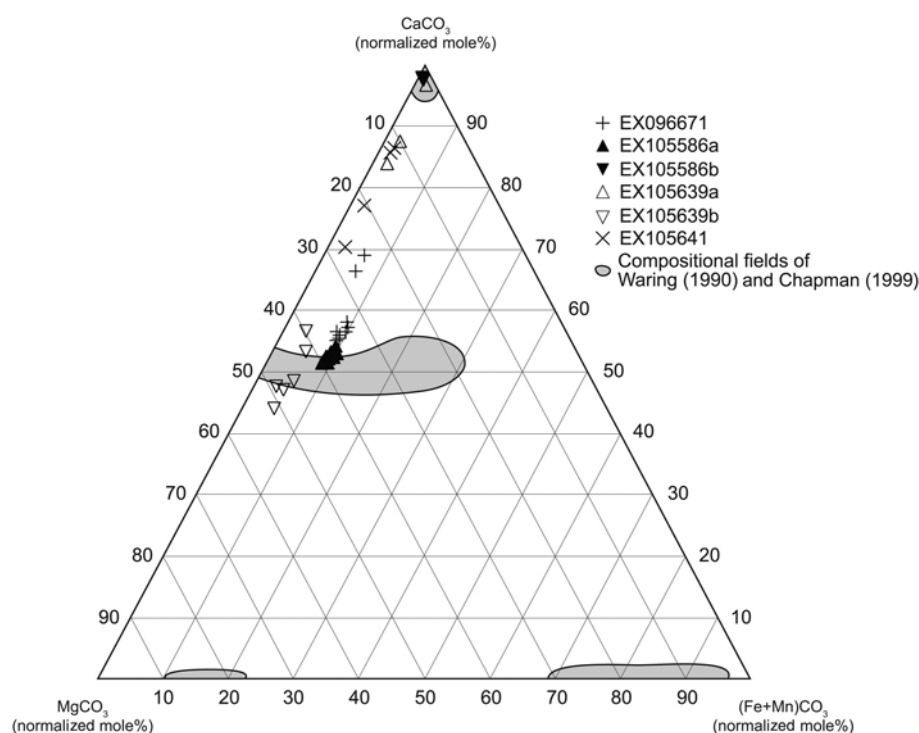


Fig. 5. Ternary diagram showing variation in chemistry of vein samples from Mount Isa Mine determined by pXRF and compositional fields determined by electron microprobe analysis (Waring 1990; Chapman 1999).

the complexity of the Mount Isa system limits the extent to which bulk geochemical methods can be used to make inferences about the mineralising systems. Nonetheless, results from Mount Isa show that pXRF analysis can be used in a qualitative manner to assess system complexity, identifying veins with multiple generations of carbonate infill and outlining areas for further characterization using laboratory techniques.

Portable X-ray fluorescence allows rapid, direct and quantitative chemical measurements of carbonate veins in the field. This adds another real-time, on-site method to collect geochemical information on which to base decisions on during drilling programs. This tool will be most powerful when used in concert with a range of techniques such as geological logging and UV fluorescence observation in the field, coupled with laboratory investigations utilizing petrographic studies and micro-analytical techniques such as EMP and LA-ICP-MS.

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References

- Barker, S., Cacho, I., Benway, H. & Tachikawa, K. 2005. Planktonic foraminiferal Mg/Ca as a proxy for past oceanic temperatures: a methodological overview and data compilation for the Last Glacial Maximum. *Quaternary Science Reviews*, **24**, 821–834.
- Bissig, T., Donoso, D., Guerra, N.C. & Dipple, G.M. 2010. Vein carbonates in the low sulfidation epithermal Au-Ag District of El Peñón, II Región, Chile: environment of formation and exploration implications. *Andean Geology*, **34**, 291–304.
- Carpenter, S.J. & Lohmann, K.C. 1992. Sr/Mg ratios of modern marine calcite: Empirical indicators of ocean chemistry and precipitation rate. *Geochimica et Cosmochimica Acta*, **56**, 1837–1849.
- Chang, L., Howie, R. & Zussman, J. 1998. *Rock-forming minerals, volume 5B: Non-silicates: Sulphates, Carbonates, Phosphates and Halides*. Geological Society, London.
- Chapman, L.H. 1999. *Geology and genesis of the George-Fisher Zn-Pb-Ag deposit, Mount Isa, Australia*. Unpublished PhD thesis, James Cook University, Australia.
- Chapman, L.H. 2004. Geology and mineralization styles of the George Fisher Zn-Pb-Ag deposit, Mount Isa, Australia. *Economic Geology*, **99**, 233–255.
- Essene, E.J. 1983. Solid solutions and solvi among metamorphic carbonates with applications to geologic thermobarometry. *Reviews in Mineralogy and Geochemistry*, **11**, 77–96.
- Fisher, L., Gazley, M.F., Baensch, A., Barnes, S.J., Cleverley, J. & Duclaux, G. 2014. Resolution of geochemical and lithostratigraphic complexity: a workflow for application of portable X-ray fluorescence to mineral exploration. *Geochemistry: Exploration, Environment, Analysis*, **14**, 149–159, <https://doi.org/10.1144/geochem2012-158>
- Gazley, M.F. & Fisher, L. 2014. A review of the reliability and validity of portable X-ray fluorescence spectrometry (pXRF) data. *Mineral Resource and Ore Reserve Estimation—The AusIMM Guide to Good Practice*, 69–82.
- Gazley, M.F., Vry, J.K., du Plessis, E. & Handler, M.R. 2011. Application of portable X-ray fluorescence analyses to metabasalt stratigraphy, Plutonic Gold Mine, Western Australia. *Journal of Geochemical Exploration*, **110**, 74–80.
- Gies, H. 1975. Activation possibilities and geochemical correlations of photoluminescing carbonates, particularly calcites. *Mineralium Deposita*, **10**, 216–227.
- Govindaraju, K. 1994. 1994 compilation of working values and sample description for 383 geostandards. *Geostandards newsletter*, **18**, 1–158.
- Hall, G.E., Bonham-Carter, G.F. & Buchar, A. 2014. Evaluation of portable X-ray fluorescence (pXRF) in exploration and mining: Phase 1, control reference materials. *Geochemistry: Exploration, Environment, Analysis*, **14**, 99–123, <https://doi.org/10.1144/geochem2013-241>
- Hannan, K.W. 1991. *Halo Project - V334: distribution of visible and carbonate, vein orientations and carbonate chemistry*. Report 1573. Carpentaria Exploration Pty. Ltd.
- Hood, S.D., Nelson, C.S. & Kamp, P.J. 2004. Burial dolomitisation in a non-tropical carbonate petroleum reservoir: the Oligocene Tikorangi Formation, Taranaki Basin, New Zealand. *Sedimentary Geology*, **172**, 117–138.
- Ichikuni, M. 1973. Partition of strontium between calcite and solution: effect of substitution by manganese. *Chemical Geology*, **11**, 315–319.
- Jenner, G.A. 1996. Trace element geochemistry of igneous rocks: geochemical nomenclature and analytical geochemistry. In: Wyman, D.A. & Bailes, A.H. (eds) *Trace element geochemistry of volcanic rocks: applications for massive sulfide exploration*. Geological Association of Canada, Short Course Notes, 51–77.
- Keith, L.H., Crummett, W., Deegan Jr, J., Libby, R.A., Taylor, J.K. & Wentler, G. 1983. Principles of environmental analysis. *Analytical Chemistry*, **55**, 2210–2218.
- Le Vaillant, M., Barnes, S.J., Fisher, L., Fiorentini, M.L. & Caruso, S. 2014. Use and calibration of portable X-Ray fluorescence analysers: application to lithogeochemical exploration for komatiite-hosted nickel sulphide deposits. *Geochemistry: Exploration, Environment, Analysis*, **14**, 199–209, <https://doi.org/10.1144/geochem2012-166>
- Morris, P.A. 2009. *Field-portable X-ray fluorescence analysis and its application in GSWA*. Geological Survey of Western Australia, Record 2009/7, 1–23.
- Mucci, A. & Morse, J.W. 1983. The incorporation of Mg²⁺ and Sr²⁺ into calcite overgrowths: influences of growth rate and solution composition. *Geochimica et Cosmochimica Acta*, **47**, 217–233.
- Page, R. & Sweet, I. 1998. Geochronology of basin phases in the western Mt Isa Inlier, and correlation with the McArthur Basin. *Australian Journal of Earth Sciences*, **45**, 219–232.
- Pearce, M.A., Timms, N.E., Hough, R.M. & Cleverley, J.S. 2013. Reaction mechanism for the replacement of calcite by dolomite and siderite: implications for geochemistry, microstructure and porosity evolution during hydrothermal mineralisation. *Contributions to Mineralogy and Petrology*, **166**, 995–1009.
- Pearson, M.J. & Nelson, C.S. 2005. Organic geochemistry and stable isotope composition of New Zealand carbonate concretions and calcite fracture fills. *New Zealand Journal of Geology and Geophysics*, **48**, 395–414.
- Perkins, W. 1984. Mount Isa silica dolomite and copper orebodies; the result of a syntectonic hydrothermal alteration system. *Economic Geology*, **79**, 601–637.
- Perkins, C., Heinrich, C.A. & Wyborn, L.A. 1999. 40 Ar/39 Ar geochronology of copper mineralization and regional alteration, Mount Isa, Australia. *Economic Geology*, **94**, 23–36.
- Piercey, S.J. & Devine, M.C. 2014. Analysis of powdered reference materials and known samples with a benchtop, field portable X-ray fluorescence (pXRF) spectrometer: evaluation of performance and potential applications for exploration lithogeochemistry. *Geochemistry: Exploration, Environment, Analysis*, **14**, 139–148, <https://doi.org/10.1144/geochem2013-199>
- Przibram, K. 1956. *Irradiation Colours and Luminescence: A Contribution to Mineral Physics*. Pergamon Press, London.
- Quye-Sawyer, J., Vandeginste, V. & Johnston, K.J. 2015. Application of handheld energy-dispersive X-ray fluorescence spectrometry to carbonate studies: opportunities and challenges. *Journal of Analytical Atomic Spectrometry*, **30**, 1490–1499.
- Reed, S.J.B. 2005. *Electron microprobe analysis and scanning electron microscopy in geology*. Cambridge University Press, Cambridge.
- Ross, P.-S., Bourke, A. & Fresia, B. 2014. Improving lithological discrimination in exploration drill-cores using portable X-ray fluorescence measurements: (1) testing three Olympus Innov-X analysers on unprepared cores. *Geochemistry: Exploration, Environment, Analysis*, 2012–2163, <https://doi.org/10.1144/geochem2012-163>
- Schulman, J.H., Evans, L.W., Ginther, R.J. & Murata, K. 1947. The Sensitized Luminescence of Manganese-Activated Calcite. *Journal of Applied Physics*, **18**, 732–739.
- Simandl, G., Stone, R., Paradis, S., Fajber, R., Reid, H. & Grattan, K. 2014. An assessment of a handheld X-ray fluorescence instrument for use in exploration and development with an emphasis on REEs and related specialty metals. *Mineralium Deposita*, **49**, 999–1012.
- Simmons, S.F., Arehart, G., Simpson, M.P. & Mauk, J.L. 2000. Origin of massive calcite veins in the Golden Cross low-sulfidation, epithermal Au-Ag deposit, New Zealand. *Economic Geology*, **95**, 99–112.
- Stone, J.G. 1959. Ore genesis in the Naica district, Chihuahua, Mexico. *Economic Geology*, **54**, 1002–1034.
- Swager, C. 1985. Syndeformational carbonate-replacement model for the copper mineralization at Mount Isa, Northwest Queensland; a microstructural study. *Economic Geology*, **80**, 107–125.
- Taylor, R. 2010. *Ore textures: recognition and interpretation*. Springer Science & Business Media, Berlin.
- Valenta, R.K. 1988. *Deformation, Fluid Flow and Mineralization in the Hilton Area, Mount Isa, Australia*. Unpublished PhD thesis, Monash University, Australia.
- Vaughan, J.R., Hickey, K.A. & Barker, S.L. 2016. Isotopic, Chemical, and Textural Evidence for Pervasive Calcite Dissolution and Precipitation Accompanying Hydrothermal Fluid Flow in Low-Temperature, Carbonate-Hosted, Gold Systems. *Economic Geology*, **111**, 1127–1157.
- Waring, C.L. 1990. *Genesis of the Mt Isa Cu Ore system*. Unpublished PhD thesis, Monash University, Australia.
- Wasylenko, L.E., Dove, P.M. & De Yoreo, J.J. 2005. Effects of temperature and transport conditions on calcite growth in the presence of Mg²⁺: implications for paleothermometry. *Geochimica et Cosmochimica Acta*, **69**, 4227–4236.
- Wilde, A., Jones, P., Gessner, K., Ailleres, L., Gregory, M. & Duncan, R. 2006. A geochemical process model for the Mount Isa copper orebodies. *Economic Geology*, **101**, 1547–1567.
- Williams, P.J. 1998. An introduction to the metallogeny of the McArthur River-Mount Isa-Cloncurry minerals province. *Economic Geology*, **93**, 1120–1131.