

Integration of Geochemical and Mineralogical Data: An Example from the Central Victorian Goldfields, Australia

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Introduction

Both geochemical and mineralogical data are collected at various stages of the resource development cycle. However, they are generally interpreted separately and often the data are collected from different samples. In some instances, geochemical data may be used to constrain quantitative X-ray diffraction (XRD) interpretations or to calculate normative mineralogy. Petrology provides important textural information and key samples may constrain parageneses, but these observations are typically qualitative. The collection of quantitative and semi-quantitative mineralogical data can be integrated with total or near-total digestion geochemical data obtained from the same samples to enhance interpretation of both data sets and provide insight into geological processes associated with hydrothermal mineralisation (e.g. Halley *et al.* 2015).

This summary will demonstrate two of the principal ways in which geochemical and mineralogical data can be integrated. The simplest approach involves attribution of mineralogical information to samples as an aid to understanding geochemical processes. A more rigorous approach makes use of quantitative and semi-quantitative mineralogical data plotted with geochemical data. The mineralogical data may include estimates of the percentages or proportions of minerals determined by quantitative XRD. It may also include spectral parameters such as the wavelength of characteristic absorption peaks for various minerals or ratios derived using those absorption wavelengths. Quantification of mineralogical data allows for full integration of mineralogical and geochemical data.

Central Victorian Goldfields

The Victorian goldfields of the western Lachlan Fold Belt of Australia have produced an estimated 2490 t of gold since 1851, most of which was recovered prior to 1920 from shallow alluvial workings and most of which was mined in central Victoria (Phillips *et al.* 2003 (Fig. 1). The majority of these deposits are typical sediment-hosted orogenic deposits containing free gold associated with structurally-controlled quartz veins, although the upper levels of the Fosterville deposit are dominated by refractory gold in arsenopyrite and pyrite that is

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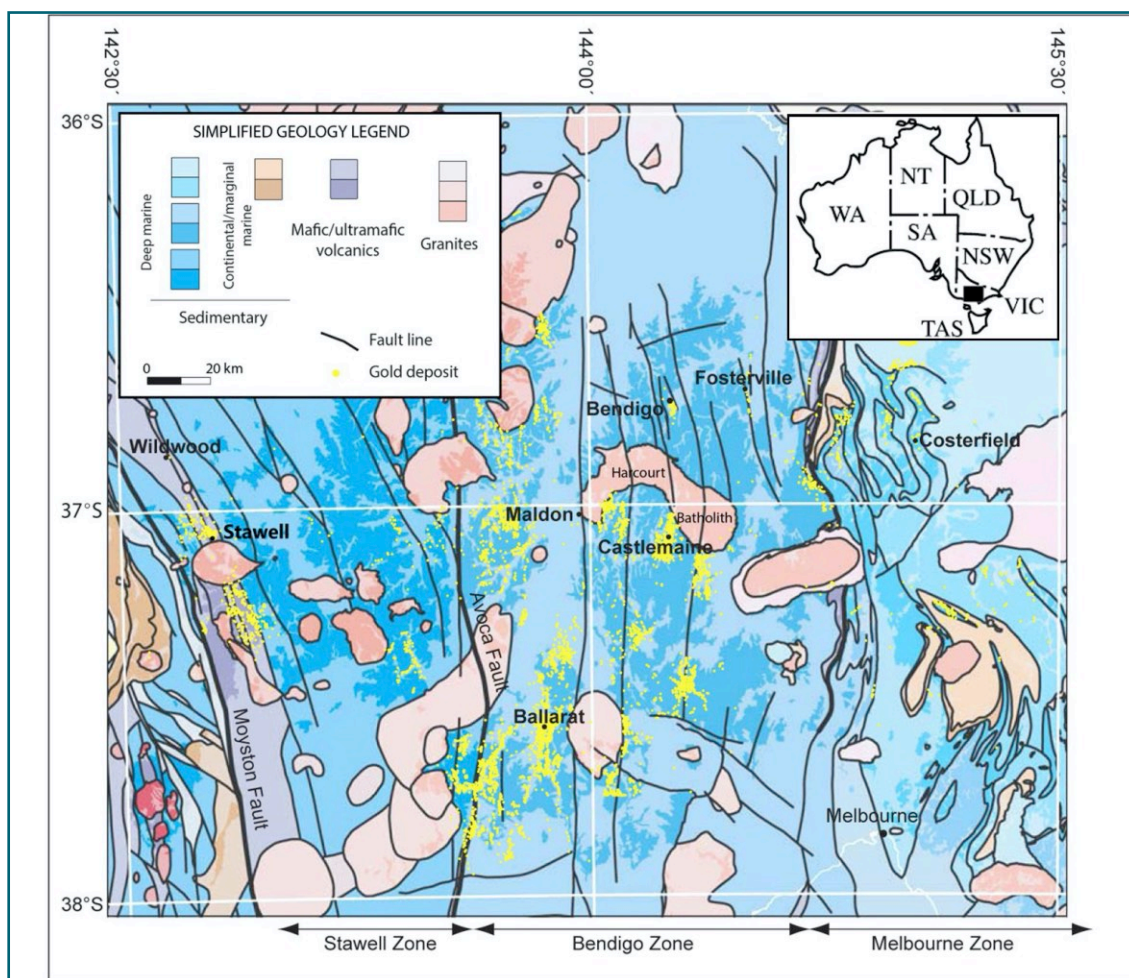


Figure 1. Paleozoic geology of the central Victorian goldfields with the locations of individual gold deposits in southeastern Australia. Darker colours for each geological unit represent exposed bedrock. Figure modified from Arne *et al.* 2016; copyright ©Geological Society of Australia, reprinted by permission of Taylor & Francis Ltd, <http://www.tandfonline.com> on behalf of the Geological Society of Australia.

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disseminated within altered metasedimentary wallrock. Geochemically, the deposits show a strong Au-As association, with variable contents of Sb and base metals.

The Victorian goldfields have seen a resurgence in exploration and mining in the last 30 years, culminating in the discovery in 2016 of high-grade gold mineralisation hosted in quartz-carbonate veins at depth in the Swan Lode at the Fosterville deposit (Fuller 2019). Several gold deposits from the central Victorian goldfields have been the subject of wallrock alteration studies that have incorporated both quantitative XRD and hyperspectral (visible to near infrared and short wave infrared) analysis of the same samples analysed geochemically (Bierlein *et al.* 2000; Arne *et al.* 2008). The integrated interpretation of the combined geochemical and mineralogical data coupled with staining of diamond drill core to reveal disseminated ferroan carbonate minerals has allowed the recognition of widespread hydrothermal alteration around many of the major deposits that is not immediately obvious (i.e. cryptic alteration).

In brief, most central Victorian gold deposits are associated with the presence of ferroan carbonate porphyroblasts, or “spots”, that increase in amount and change to a more ferroan composition as mineralised structures are approached (Bierlein *et al.* 1998, 2000; Arne *et al.* 2008). Dugdale *et al.* (2009) suggest the earliest carbonate spots are of diagenetic origin and not associated with gold mineralisation. Host sandstones are also characterised by Na loss associated with the destruction of detrital albite and the formation of hydrothermal white mica with a muscovite composition (Arne *et al.* 2008, 2016), as well as kaolinite in the case of Ballarat. Elevated concentrations of chalcophile elements, particularly As and Sb, are associated with disseminated pyrite, with arsenopyrite developed proximal to mineralised structures (Bierlein *et al.* 1998, 2000; Arne *et al.* 2008). Stibnite occurs in quartz veins at Costerfield and Fosterville. Recognition of these alteration types provides an important tool for vectoring towards mineralised structures in the central Victorian goldfields.

Integration with Quantitative XRD Data

Bierlein *et al.* (2000) presented the results of quantitative XRD analysis of pulps for typical wallrock samples without veining at several central Victorian goldfields. These samples were also analysed geochemically using X-ray fluorescence (XRF) following a total fusion digestion. These data have been supplemented with quantitative XRD and geochemical data from the Bendigo goldfield in Swan (2002). The XRD results allow the geochemical data to be interpreted within a mineralogical framework and provide clear evidence of the mineralogical changes that occur during wall alteration in central Victorian gold deposits.

Figure 2 compares major elements with quantitative mineralogy from six different central Victorian goldfields, with

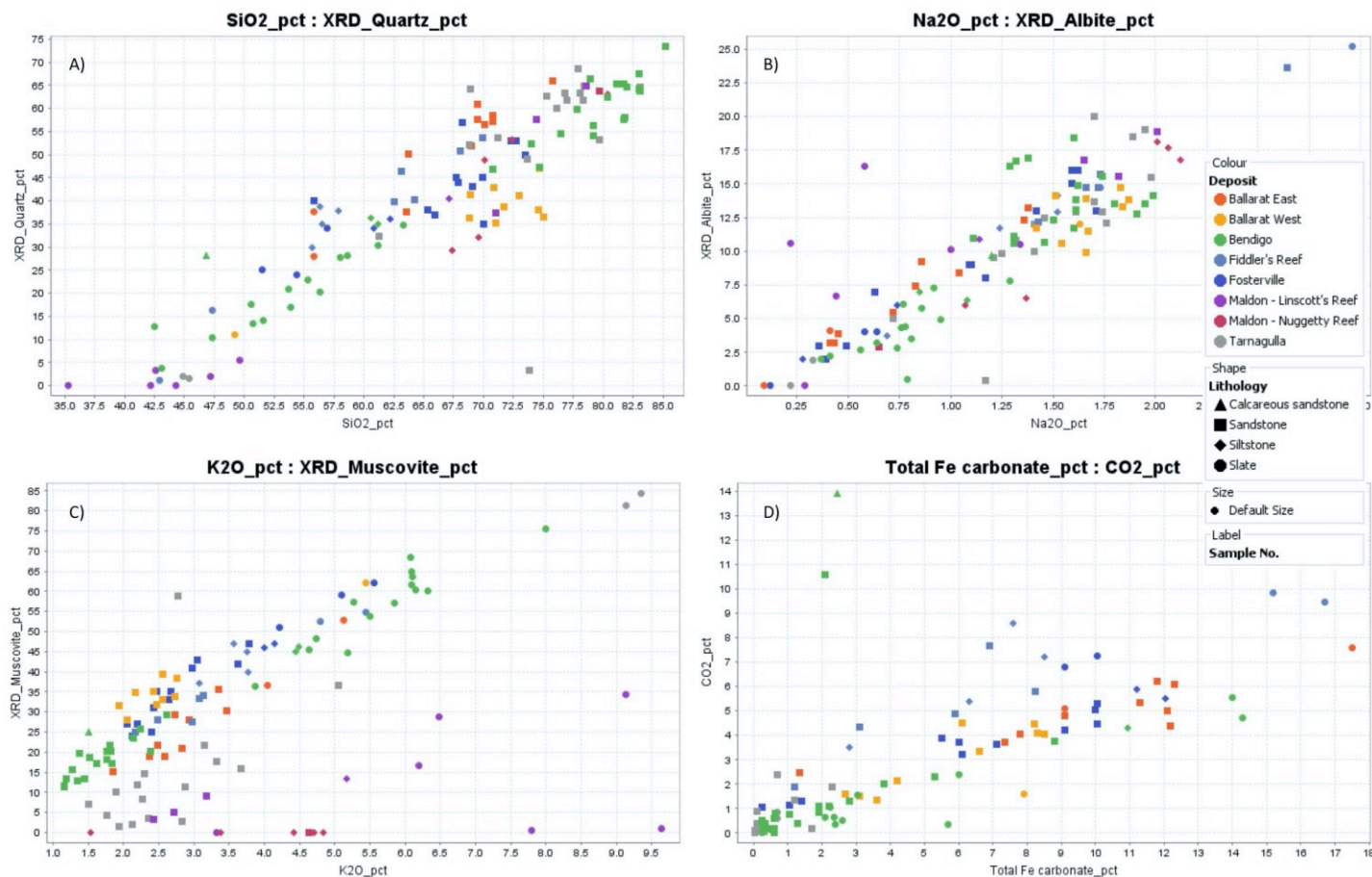


Figure 2. Scatter plots illustrating the relationships between major elements and quantitative XRD mineralogy. $N = 127$.

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some distinction for different zones within Maldon and Ballarat. In general, there is a positive correlation between SiO_2 , Na_2O , K_2O and CO_2 with quantitative XRD estimates of quartz, albite, muscovite and total ferroan carbonate (siderite + ankerite), respectively. Spearman Rank correlation coefficients vary from 0.88, 0.86, 0.55 and 0.87, respectively, for the geochemical and mineralogical data. Weak correlation between K_2O and muscovite is caused by the presence of samples from Maldon (Fig. 2c), in which the alteration assemblages have been affected by contact metamorphism, resulting in biotite as a significant K-bearing mineral. The Spearman Rank correlation for K_2O and muscovite increases to 0.85 if the data from Maldon are removed from the analysis. Two samples from Bendigo also plot off the trend defined by CO_2 and total ferroan carbonate due to the presence of calcareous sandstone samples (Fig. 2d). Figure 2 also illustrates the fundamental control on both geochemistry and mineralogy exerted by lithology, with slates generally having the highest contents of ferroan carbonate and muscovite, and the sandstones the highest contents of quartz and detrital albite.

Figure 3 illustrates trends in selected quantitative XRD mineralogy with respect to the lateral distance of the

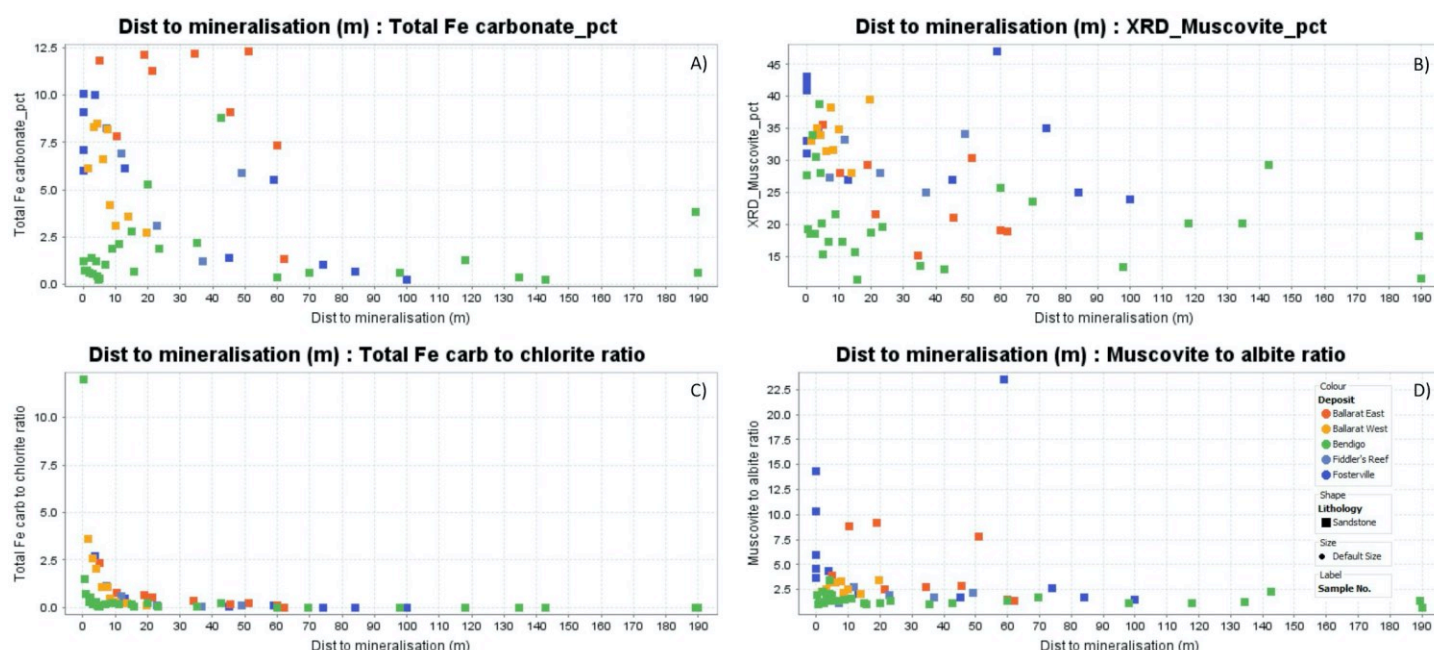


Figure 3. Scatter plots illustrating the relationship between distance of the samples from a mineralised structure and quantitative XRD mineralogy. $N = 62$.

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samples from mineralised structures. Data from Maldon and Tarnagulla have been excluded, as both contain alteration assemblages that have been overprinted by contact metamorphism. The analysis has also been restricted to sandstone lithologies to minimise mineralogical variability related to lithology. There is considerable scatter in the mineralogical data (Fig. 3a and 3b) that reflects the variability in the degree to which wallrock samples are altered, in response to fluid-rock interactions controlled by local permeability. However, clear trends of increasing ferroan carbonate and muscovite are apparent with increasing proximity to mineralised structures when these minerals are ratioed against chlorite and albite, respectively (Fig. 3c and 3d). Whether ferroan carbonates replace chlorite, or whether chlorite represents an outer, more distal alteration assemblage is not clear. What is clear is that, aside from the Bendigo goldfield, chlorite is not a stable alteration phase proximal to the mineralised structures examined.

Integration with Hyperspectral Data

Arne *et al.* (2008) undertook further analyses of wallrock alteration in fresh core samples at six central Victorian goldfields. Samples were analysed mainly by a combination of 4-acid digestion with an ICP-ES/MS finish, with Au determined by fire assay/ICP-MS, carbonate C determined by LECO analyser and Ti, W, Ba and Zr determined by pressed pellet XRF. A separate 50 g split of <2 mm crush material was loaded into a plastic chip tray and analysed using a HyChips™ robotic table at the Commonwealth Scientific and Industry Research Organisation (CSIRO). The HyChips™ collects information on absorption by hydrous, oxide and carbonate minerals in the visible to near-infrared (VNIR) and short wave infra-red (SWIR) part of the electromagnetic energy spectrum. The data were analysed by AusSpec International using The Spectral Geologist™ software, also developed by CSIRO. The mineralogical data are summarised in terms of mineral assemblages ordered with respect to relative spectral intensity in each sample.

The relationship between the position of the AIOH absorption peak measured in the SWIR range (wavWMica) and As is illustrated in Figure 4, excluding Maldon and Castlemaine samples. The position of this peak is sensitive to white mica composition, specifically the substitution of Al by Fe²⁺ and/or Mg in the white mica structure (Tappert *et al.* 2013). The use of As is preferred as a measure of alteration over the distance to mineralisation as higher concentrations of As indicate interaction with a hydrothermal fluid. The dashed lines on the diagrams provide a general boundary between white

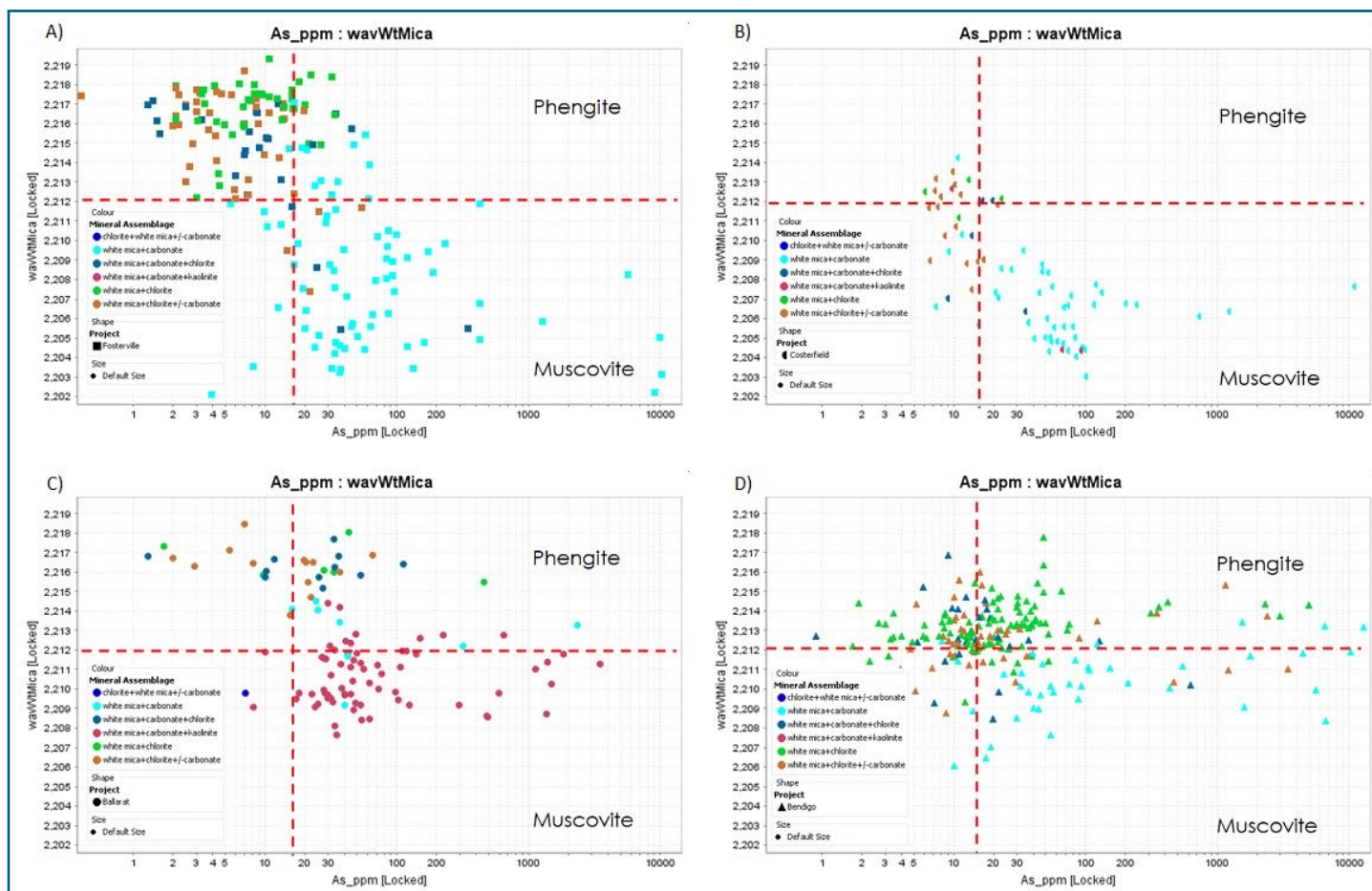


Figure 4. Scatter plots illustrating the relationship between the wavelength position of the AIOH absorption peak in white mica (in nanometres) and arsenic concentration for: a) Fosterville, b) Costerfield, c) Ballarat and d) Bendigo.

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micas of dominantly phengite composition, in which there is some substitution of Al by Fe^{2+} and/or Mg, and muscovite compositions, in which this substitution is minimal. The dashed line for As at approximately 15 ppm represents a lower threshold evident in some of the data, below which samples show no evidence of hydrothermal alteration.

White mica – ferroan carbonate assemblages are dominated by muscovite at Ballarat, Bendigo, Costerfield and Fosterville. The alteration assemblage at Ballarat also includes kaolinite (Fig. 4c), even though the samples were collected well below the base of oxidation in the goldfield. Samples that contain more phengitic white mica compositions are dominated by white mica and chlorite, with minor carbonate in some cases. The use of an upper As threshold of 100 ppm excludes most phengite-bearing samples at Ballarat, Costerfield and Fosterville, indicating that phengite generally does not persist in those samples with the strongest evidence for hydrothermal alteration. Although a trend to lower AlOH absorption wavelengths is apparent in the data from Bendigo (Fig. 4d), the relationship between white mica composition and As concentration is not as clear as at the other three deposits shown. Chlorite-bearing samples at Bendigo may have elevated As levels, as previously determined by Swan (2002).

A useful diagram for tracking feldspar-destructive alteration is the K/Al versus Na/Al molar ratio plot of Davies & Whitehead (2006) (Fig. 5). The progressive loss of Na with destruction of detrital albite in fresh sandstone samples follows the albite-muscovite tie line and is associated with an addition of K. The mineralogy inferred from geochemical trends and nodes on the diagram is supported by the hyperspectral alteration assemblages determined for the samples.

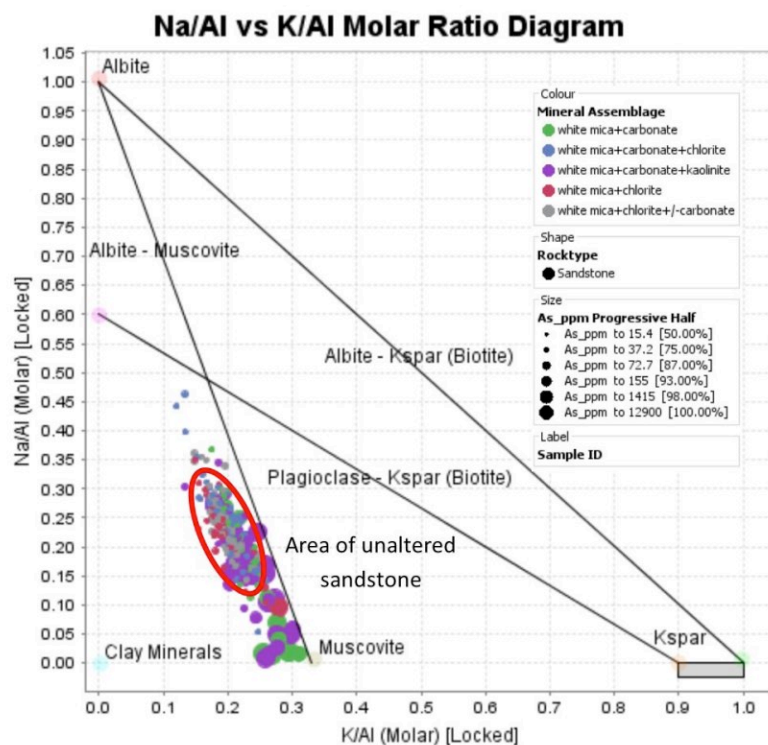


Figure 5. Molar plot for Na/Al versus K/Al modified from Davies & Whitehead (2006) combined with proportional dot plot of As concentration showing the trend in sandstone samples of decreasing Na with increasing As content for samples from Ballarat, Castlemaine, Fosterville and Costerfield. Data from Maldon and Bendigo have been excluded.

The presence of chlorite and/or kaolinite would drive the samples towards the origin, were they present in significant quantities, but this is not indicated by the geochemical data. Data from Maldon have been excluded due to contact metamorphic overprinting. Data from Bendigo have also been excluded because chlorite-bearing assemblages show enrichment in As, and this is not the case in the other central Victorian goldfields investigated. In general, sulphidation is spatially associated with albite destruction and the formation of muscovite.

Discussion

Although not illustrated in Figure 3a, the general increase in ferroan carbonate is also evident if data for siderite and ankerite are plotted independently. Electron microprobe analyses of carbonate spots in Fosterville samples indicate that these two carbonate types represent two distinct compositional populations (Arne *et al.* 1998) and that “siderite” in fact represents an intermediate composition between siderite and magnesite. Geochemical data from central Victorian goldfields are also consistent with an increase in the Fe content of ferroan carbonates with increasing As content (Arne *et al.* 2008). The spatial trends illustrated in Figure 3 and documented in Arne *et al.* (2008) suggest that the distribution of ferroan ankerite is controlled by hydrothermal fluids and unlikely to be a diagenetic feature, as suggested by Dugdale *et al.* (2009), although diagenetic calcite may be present in distal samples.

Feldspar-destructive alteration in sandstones provides a useful additional vector for indicating proximity to mineralised

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structures in fresh rock using either total or near-total digestion geochemical analyses, hyperspectral data, or quantitative XRD analyses once the background lithological effects are accounted for. Shales contain little detrital albite and thus do not display the shift in white mica composition characteristic of sandstones. A preference for sampling sandstone has thus characterised the work of Bierlein *et al.* (2000) and Arne *et al.* (2008), but risks missing elevated ferroan carbonate in shales, as demonstrated by Swan (2002) at Bendigo.

The use of ICP-MS analyses of chalcophile elements such as Au, As and Sb should also not be discounted, as disseminated pyrite grains spatially associated with mineralised structures are often enriched in these elements and can be detected by lithogeochemical sampling. The hydrothermal nature of these pyrite grains or overgrowths is indicated by sulphur isotopic values near 0 per mil (Bierlein *et al.* 2004).

There remains a fundamental difference in alteration assemblages at Bendigo and, to lesser extent, Castlemaine, with those documented at Ballarat, Fosterville and Costerfield. These differences may relate to a different timing of mineralisation (Wilson *et al.* 2020). Gold mineralisation at Bendigo is estimated to have occurred at ca. 445 Ma based on $\text{Ar}^{40}/\text{Ar}^{39}$ age determinations of hydrothermal white mica and Re-Os analyses of hydrothermal sulphide minerals (Arne *et al.* 2001; Phillips *et al.* 2003, 2012), and a similar timing can be inferred for the Castlemaine goldfield. The timing of gold mineralisation at Ballarat is also considered to have commenced at ca. 445 Ma, also based on $\text{Ar}^{40}/\text{Ar}^{39}$ age determinations of hydrothermal white mica, but there is also evidence for a latter mineralising episode or remobilisation of gold around 370 Ma (Phillips *et al.* 2003, 2012). The Fosterville and Costerfield gold deposits are demonstrably younger than the Bendigo deposit (Phillips *et al.* 2003). Gold mineralisation occurs in rocks of Silurian age at Costerfield and $\text{Ar}^{40}/\text{Ar}^{39}$ age determinations of hydrothermal white micas and U-Pb age determinations of inherited zircon grains in felsic dykes at Fosterville suggest a Devonian age for Au mineralisation (Bierlein *et al.* 2001). Thus, it appears that Au deposits in central Victoria have formed at different stages of the Lachlan Orogen with subtly different wallrock alteration styles and patterns, perhaps related to different ambient temperatures at the time of gold emplacement or to the geochemical and/or physical characteristics of the hydrothermal fluids.

Conclusions

The case study presented here illustrates a simple but effective approach to the integration of geochemical and mineralogical data using both descriptive mineralogy and quantitative results. This process necessarily begins with the collection of both data types from the same samples and requires geochemical and mineralogical data to be merged into a common data file for interpretation. Quantitative mineralogical data can be incorporated into statistical or geospatial evaluations of geochemical data to provide insight into the mineralogical controls on geochemical results. The integration of geochemical and mineralogical data therefore provides a more comprehensive understanding of wallrock alteration processes, as illustrated by the results of studies carried out within the central Victorian goldfields.

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