

Three mechanisms of ore re-mobilisation during amphibolite facies metamorphism at the Montauban Zn–Pb–Au–Ag deposit

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Abstract The relative importance of mechanical re-mobilisation, hydrothermal dissolution and re-precipitation, and sulphide melting in controlling redistribution of metals during concurrent metamorphism and deformation is evaluated at the middle amphibolite facies Montauban deposit in Canada. As at many other deposits, ductile deformation was important in driving mechanical re-mobilisation of massive sulphides from limb regions into hinge regions of large-scale folds and is thus the most important for controlling the economics of Pb and Zn distribution. Two possible stages of hydrothermally driven re-mobilisation are discussed, each of which produces characteristically different alteration assemblages. Prograde hydrothermal re-mobilisation is driven by pyrite de-sulphidation and concurrent chlorite dehydration and is thus an internally driven process. At Montauban, the H₂S-rich fluid generated through this process allowed re-mobilisation of gold into the wall rock, where it was deposited in response to sulphidation of Fe Mg silicates. Retrograde hydrothermal re-mobilisation is an externally driven process, whereby large volumes of fluids from outside the deposit may dissolve and re-precipitate metals, and cause hydration of silicate minerals. This second hydrothermally driven process is not recognised at Montauban. Sulphide melting

occurred as temperatures neared the peak metamorphic conditions. Melting initiated in the massive sulphides through arsenopyrite breakdown, and a small volume of melt was subsequently re-mobilised into the wall rock. Trace element partitioning and fractional crystallisation of this melt generated a precious metal-rich fractionate, which remained mobile until well after peak metamorphism. Thus, prograde hydrothermal re-mobilisation and sulphide melting were the most important mechanisms for controlling the distribution of Au and Ag.

Keywords Mechanical re-mobilisation · Hydrothermal re-mobilisation · Ore metamorphism · Sulphide melt · Grenville province

Introduction

The Montauban Zn–Pb–Au–Ag deposit is located 100 km west of Quebec City in the Grenville Province of southern Quebec, Canada (Fig. 1a). It was mined sporadically between 1910 and the 1980s, and has more recently been of interest because of Au–Ag mineralisation that occurs adjacent to the massive Zn–Pb sulphides. It was metamorphosed at mid-amphibolite facies conditions (Stamatelopoulou-Seymour and MacLean 1984; Bernier et al. 1987) during the Grenvillian Orogeny (ca. 980–1080 Ma; Gower and Krogh 2002). Another deposit with striking similarities to Montauban is also found within the Grenville Province. Calumet is located 90 km northwest of Ottawa in Canada and is also thought to be a volcanic massive sulphide (VMS) deposit that was metamorphosed at 650–700°C and 4–6 kbar (Williams 1990a). It has been suggested that Au at Calumet was introduced after peak metamorphism (Williams 1990a,b). In contrast, gold mineralisation at Montauban is thought to

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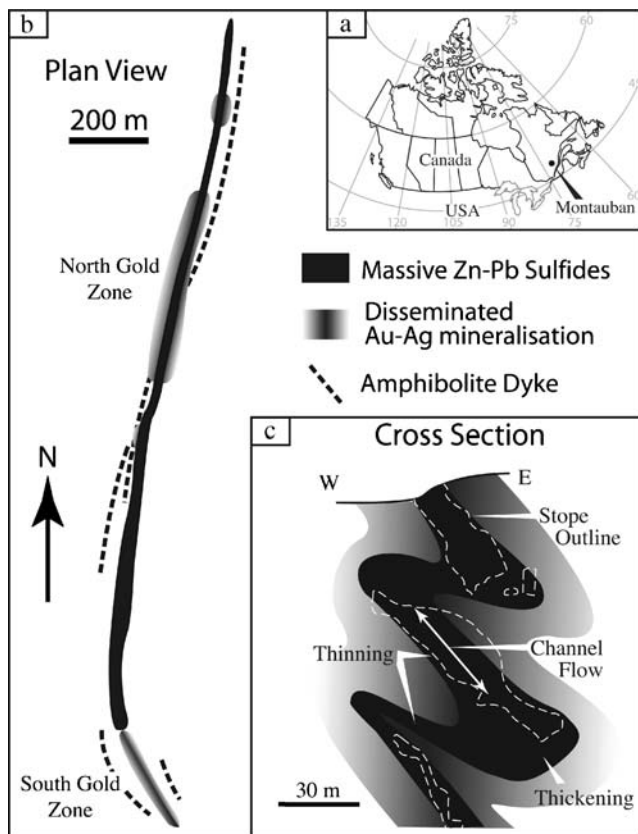


Fig. 1 **a** Location of the Montauban deposit. **b** Plan view of the deposit showing the projected to surface geometry of the ore body (modified from Bernier et al. 1987; Jourdain 1993). **c** Schematic cross-section highlighting the pre-mining morphology of the massive sulphides. The position of a late cross-cutting mafic dyke has been removed to estimate the original morphology. Modified from Jourdain (1993)

have been part of the initial exhalite ore, deposited concurrently with the Zn–Pb–Ag sulphides (Bernier et al. 1987). This deposit is thus potentially a useful location to investigate metal re-mobilisation in Au-bearing massive Zn–Pb sulphides.

Because most massive Pb–Zn deposits form in basal environments, nearly all deposits that are mined have been metamorphosed and deformed to some degree. Some, such as McArthur River and Century in Australia, are only very slightly metamorphosed and deformed. Others, such as Broken Hill, also in Australia, have been metamorphosed at granulite facies conditions and have concurrently undergone complex multigenerational deformation. It is this combination of higher temperatures and deformation that promotes re-mobilisation of ore material.

Ore re-mobilisation is clearly important to miners and near-mine explorationists because it promotes, in many deposits, localisation of larger and sometimes richer volumes of ore material. In some deposits ore re-mobilisation has transformed an uneconomic deposit into an economic one. Clearly,

understanding the processes that cause re-mobilisation allows prediction of metal distribution.

Previous workers have investigated individual aspects of ore re-mobilisation at different deposits. There have been disputes over when to use the terms mobilisation and re-mobilisation. Marshall et al. (2000) indicate that “re-mobilisation” should be used when referring to translocation of mineralisation in and around a pre-existing semi-massive ore deposit. There are three possible mechanisms by which ore material can be re-mobilised after it has formed: mechanical re-mobilisation, hydrothermal dissolution and re-precipitation, and transfer of a sulphide melt (reviewed by Marshall et al. 2000). Generally, researchers have focussed on describing one particular re-mobilisation mechanism. This is the first attempt to investigate the efficacy of all three mechanisms within one deposit. This paper investigates how each of these processes has affected the distribution of various ore components.

Geology of the Montauban Zn–Pb–Au–Ag deposit

Montauban is situated within an extensively folded sequence of amphibolite facies rocks that are sandwiched between intrusions of granodioritic to gabbroic composition. In the mine area, these metamorphic rocks strike roughly north–south and dip $\sim 60^\circ$ to the east and consist of migmatitic biotite gneiss, amphibolite, quartzofeldspathic biotite gneiss and quartzite. Locally, the Montauban ore is contained within a thin complex package of biotite gneiss, nodular sillimanite gneiss, cordierite–anthophyllite gneiss, calc-silicate rocks (containing small massive pods of scapolite) and rocks interpreted by Bernier et al. (1987) as meta-exhalites (tourmalinite and, along strike, iron formation and carbonate rocks).

Ore at Montauban was considered to be pyrometasomatic (i.e. metamorphogenic) in origin (Alcock 1930; Osborne 1939), but all recent researches have suggested that mineralisation represents metamorphosed massive to semi-massive sulphides that initially formed in an exhalative environment (Sangster 1972; Stamatelopoulou-Seymour and MacLean 1977, 1984; Bernier et al. 1987). Peak metamorphic conditions were estimated by Bernier et al. (1987) to have been 650°C , 6 kbar, $f_{\text{O}_2}=10^{-17}$ bar and $f_{\text{S}_2}=10^{-2}$ bar, which is similar to $630\text{--}650^\circ\text{C}$ and 4.9 ± 0.4 kbar, the estimate of Stamatelopoulou-Seymour and MacLean (1984).

Mining at the Montauban deposit has been sporadic. From 1911 to 1955 and again in 1961, 2.7 Mt of massive sulphide ore (grading 4.5% Zn, 1.5% Pb, 0.56 g/t Au, 70 g/t Ag) was mined from the Tetreault mine, and 102,000 t (grading 2.9% Zn, 0.9% Pb, 34 g/t Ag) of massive sulphide ore was extracted from the Montauban Anacon mine from 1953 to 1954 (M. Gauthier, personal communication). Consequently, this part of the ore can now only be observed at sporadic

weathered surface outcrops. Massive ore is composed of coarse-grained sphalerite, galena, pyrrhotite, pyrite and chalcopyrite with minor cubanite, tetrahedrite and molybdenite (Stamatelopoulou-Seymour and MacLean 1984).

Marginal to the massive sulphide ore (Fig. 1b), in two separate zones (a north and a south zone), is a small volume of Au–Ag mineralisation within a package of gahnite-bearing gneiss, although the highest Au grades are found within the massive sulphides (Bernier et al. 1987). Some Au and Ag have been produced from the marginal mineralisation. From 1983 to 1987, 330,830 t of ore (grading 4.27 g/t Au, 12.45 g/t Ag) was extracted from the North gold mine, and from the South gold mine 225,433 t of ore (grading 3.70 g/t Au, 72.37 g/t Ag) was extracted between 1987 and 1990 (M. Gauthier, personal communication). This mineralisation consists of disseminated pyrrhotite, galena, sphalerite and chalcopyrite with a large range of minor sulphides, sulphosalts and native minerals (Bernier et al. 1987).

Disseminated Au–Ag mineralisation at Montauban was interpreted by Bernier et al. (1987) to be part of a metamorphosed siliceous exhalite. This is considered to be a reasonable interpretation for several reasons: (1) peak-metamorphic silicate minerals contain numerous sulphide inclusions indicating that the sulphides were present during peak metamorphism; (2) there are many examples of disseminated sulphides (including Au-bearing minerals) where hydrothermal alteration does not overprint the metamorphic phases, indicating that mineralisation predates metamorphism; and (3) as will be discussed in detail, Zn and Pb are not easily re-mobilised into disseminated sulphide zones, so their presence in abundance in some parts of the Au zones suggests that they were part of a pre-existing mineralised region.

Materials and methods

Because the massive sulphide part of the Montauban deposit has been mined, access to samples from this part of the ore body is restricted. Some weathered samples of massive sphalerite–galena–pyrrhotite ore were obtained from surface exposures, but drill core of this material was not available. A simplistic evaluation of mechanical mobilisation of massive sulphides was conducted at large scale, through analysis of the previously reported cross-sectional shape of the ore body. The highly re-crystallised nature of the massive sulphides reported previously (Jourdain et al. 1987) was confirmed through thin section examination. Several samples lacking sulphide mineralisation were also collected on the surface to characterise the variation in near-ore lithologies.

Several diamond drill cores through disseminated sulphides that had high gold assays from the North and South gold zones were sampled to characterise the disseminated gold mineralisation. Twenty-four samples were collected in all. Thin sections of the samples were analysed by reflected light microscopy and electron microprobe, and several samples were analysed (through a commercial lab) by X-ray fluorescence (XRF) for whole-rock compositions. Electron microprobe analyses for various ore minerals identified at Montauban were previously reported in Tomkins et al. (2006). XRF analyses were reported in Tomkins et al. (2007).

Using the JEOL JXA8200 electron microprobe at the University of Calgary, local bulk compositions for 11 small accumulations of crystallised sulphide melt (see Sulphide Melting at Montauban, below) were obtained. This was done by taking a BSE image of each accumulation and obtaining a wavelength-dispersive spectrometry analysis of each mineral therein. Approximate bulk compositions for each accumulation were derived using Adobe Photoshop to calculate the area of each analysed mineral in each BSE image. These local bulk composition data are presented in Table 1. This technique cannot provide an exact local bulk composition because only a two-dimensional section through each sulphosalt accumulation is examined.

Mechanical re-mobilisation of massive sulphides

Observations

The massive sulphide ore body at Montauban is clearly deformed. The southern end has been subject to open folding, as seen in plan view (Fig. 1b), and in cross-section, it has the gross architecture of a series of slightly overturned tight z-folds (Fig. 1c). Jourdain et al. (1987) interpreted three episodes of deformation to have affected the deposit. D_1 was thought to have been an isoclinal transposition event. The S_1 fabric produced at this stage wraps around the z-folds seen in Fig. 1c, which thus represent D_2 deformation. The third deformation was invoked to explain additional complexities in the structural pattern of the area and would include the open folding seen in Fig. 1b. Deformation of the massive sulphides at Montauban has changed the thickness of different parts of the ore body. Limb regions of folds are attenuated, whereas hinge regions are thickened (Fig. 1c).

Much of the ore is re-crystallised and does not show the structural fabric that is preserved in the surrounding silicate rocks (Jourdain et al. 1987). However, evidence of mild deformation is preserved in some localities, such as kink bands in pyrrhotite, and bent cleavage planes in galena (Stamatelopoulou-Seymour and MacLean 1984).

Table 1 Local bulk compositions of crystallised melt accumulations plotted on Fig. 4

Accumulation number	1	2	3	4	5	6	7	8	9	10	11
S	9.55	13.06	12.97	15.25	5.91	10.78	7.84	9.56	11.30	11.37	7.00
As	5.37	0.67	8.90	8.87	0.18	3.83	3.93	0.33	4.21	0.03	0.00
Sb	11.90	15.03	8.59	16.84	14.04	12.18	14.42	13.58	8.06	5.24	6.54
Pb	41.04	36.37	28.26	31.72	35.36	47.28	28.68	52.30	53.35	70.01	0.40
Hg	0.00	0.02	0.01	0.02	0.03	0.04	0.02	0.04		0.00	
Au	1.41	1.36	0.00	0.99	0.36	0.00	3.51	0.00	1.29	0.05	39.67
Ag	25.86	29.57	30.77	10.26	43.57	22.59	36.82	21.52	16.18	12.57	35.61
Zn	0.02	0.13	0.00	0.02	0.01	0.00	0.07	0.00	0.33	0.01	
Cu	0.87	2.71	0.01	0.25	0.14	0.01	1.19	0.01	1.60	0.00	0.00
Fe	3.63	1.09	10.50	15.79	0.38	3.29	3.54	2.66	3.21	0.00	10.80
Bi	0.36									0.72	
Sn									0.47	0.01	
Total	100.00	100.00	100.00	100.00	99.97	100.00	100.00	100.00	100.00	100.00	100.01
Pb/Ag+Au	1.50	1.18	0.92	2.82	0.80	2.09	0.71	2.43	3.05	5.55	0.01
Pb/Sb	3.45	2.42	3.29	1.88	2.52	3.88	1.99	3.85	6.62	13.37	0.06
As/Sb+Ag+Au	0.14	0.01	0.23	0.32	0.00	0.11	0.07	0.01	0.16	0.00	0.00
Fe/Sb+Ag+Au	0.09	0.02	0.27	0.56	0.01	0.09	0.06	0.08	0.13	0.00	0.13

Discussion

Mechanical re-mobilisation has been reviewed in detail by Marshall et al. (2000). There are a range of mechanisms by which sulphides may flow during deformation, including cataclasis and granular flow, dislocation flow and diffusive mass transfer. Each of these mechanisms may be active at the same time within a deforming heterogeneous package of sulphides because of the differing mechanical properties of each sulphide mineral. For example, whilst pyrite is deforming and being re-mobilised through cataclasis, galena may deform through a combination of dislocation flow and diffusive mass transfer. This flow is essentially in the solid state, though it is facilitated, in most cases, by the presence of a hydrothermal fluid (Marshall et al. 2000). The principal factor that causes massive sulphides to deform and be re-mobilised relative to surrounding silicate rocks is that they are more ductile than silicate minerals (Marshall and Gilligan 1993). Sulphides thus partition strain, focusing the majority of deformation into the massive sulphide body and away from the silicate rocks.

Mechanical re-mobilisation is particularly effective at redistributing massive sulphides but ineffective in re-mobilising disseminated sulphides any significant distance. This is because a thick body of massive sulphide acts as a single unit that is much more ductile than the surrounding silicate rocks. Strain is partitioned through the entire unit allowing it to act as a single mobile body, and causing essentially channelised flow. Each single grain of sulphide in disseminated ore acts the same way, but only migrates to the nearest relatively dilational site, such as into the

pressure shadow of a garnet porphyroblast. Thus in disseminated ore, mechanical re-mobilisation happens on the centimeter scale, whereas in massive sulphides, it can occur on the scale of tens of meters (Marshall et al. 2000).

The ore body morphology is likely to have developed through partitioning of strain into the massive sulphide body. Strain is partitioned in this way because under mid-amphibolite facies conditions sphalerite, galena, chalcopyrite and pyrrhotite are more easily deformed than silicates (Marshall and Gilligan 1993). The fold limb regions experience shear deformation and become compressional regions, whereas fold noses act as dilational zones. Therefore, at Montauban, sulphides migrated from the limbs through channelised flow into the fold hinges causing thickening at the latter.

At low temperature conditions, galena is able to deform in a ductile fashion, whilst the other sulphides, particularly pyrite, deform in a brittle fashion (Marshall and Gilligan 1993). Consequently, galena can be preferentially re-mobilised into specific structural sites under these conditions. However, at amphibolite facies conditions, sphalerite, chalcopyrite and pyrrhotite also deform in a ductile fashion and are more ductile than most silicate minerals. Thus, at this metamorphic grade, massive sulphides tend to migrate as a whole unit, including minor interstitial silicate phases such as gahnite, and there is little or no mechanical fractionation of the ore. At Montauban, areas into which massive sulphides were re-mobilised by mechanical flow are therefore unlikely to have experienced relative enrichment in any particular metal when compared with the original ore body.

Prograde hydrothermal re-mobilisation of gold

Observations

Within the disseminated sulphides of the North and South gold zones, the majority of sulphide grains are observed to be situated at grain boundaries between silicate minerals and do not disrupt the metamorphic fabric. However, some sulphide minerals are also associated with alteration centered around cross-cutting microfractures. These narrow zones of hydrothermal alteration are compatible with amphibolite facies conditions (e.g. Spear 1993), consisting variously of tremolite, anthophyllite/gedrite and phlogopite (Fig. 2a). Pyrrhotite and gold mineralisation is observed in intimate association with these alteration zones (Fig. 2b and c). It can be seen in Fig. 2b that this alteration overprints the structural fabric.

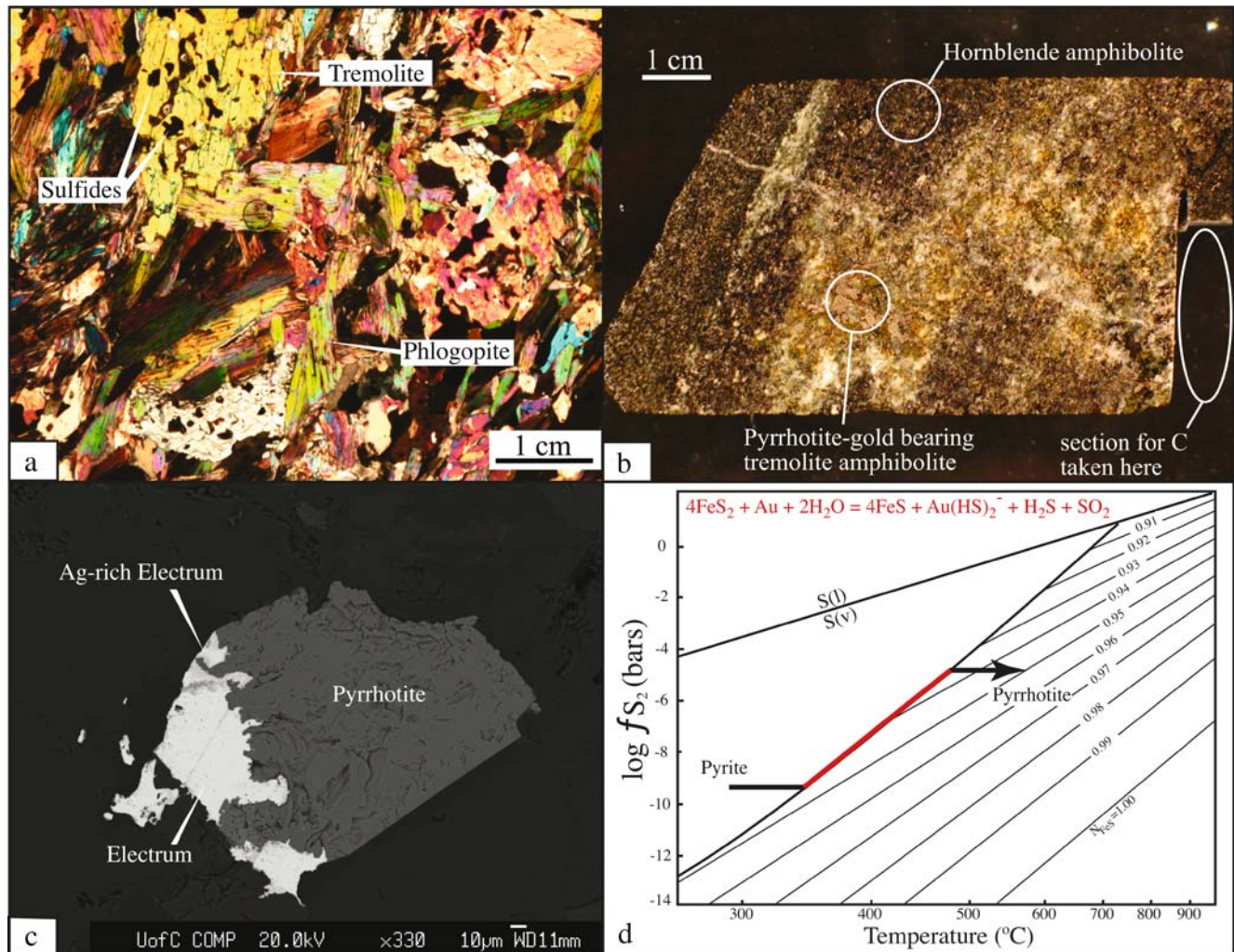


Fig. 2 Pre- to syn-peak metamorphic hydrothermal alteration of amphibolite and consequent sulphidation in the wall rock at Montauban. **a** Photomicrograph showing tremolite–phlogopite alteration in detail. **b** Drill core showing dark coloured hornblende being replaced by tremolite + pyrrhotite. Note the position from which a thin

Wider zones, up to several meters across, with tremolite or anthophyllite/gedrite and/or phlogopite are also observed that contain disseminated pyrrhotite, chalcopyrite, sphalerite and galena. In many places, these amphibole and mica grains are aligned parallel to the dominant foliation.

Discussion

The most important metamorphic reaction amongst sulphides for hydrothermal re-mobilisation, particularly in relation to gold, involves pyrite de-sulphidation:



This is principally because pyrite is the dominant sulphide in many deposit types before metamorphism. It therefore contributes the largest proportion of sulphur of any mineral consumed on the prograde path. This reaction

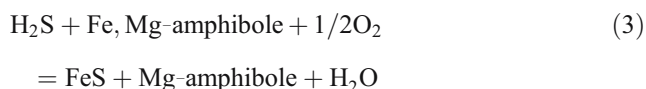
section has been taken. **c** Back-scattered electron image (from an electron microprobe) showing an intimate association between electrum and pyrrhotite in the same sample. **d** Log fS_2 -temperature diagram showing how desulphidation of pyrite proceeds during metamorphism (Modified from Toulmin and Barton 1964)

can start at a range of temperatures, depending on the background sulphur fugacity (Fig. 2d; Toulmin and Barton 1964). However, the amount of sulphur that can be dissolved in water remains low until the lower amphibolite facies is reached (Connolly and Cesare 1993). With increasing temperature in the amphibolite facies sulphur is rapidly stripped from pyrite through reactions such as:



Transition into the lower amphibolite facies also coincides with liberation of considerable volumes of water through chlorite dehydration. Consequently, this will be the stage when much of the pyrite present in a deposit will break down. Nevertheless, some pyrite remains to higher temperatures within massive sulphide deposits for two reasons. Firstly, there is often simply more pyrite present to be broken down. This is relevant because the amount of pyrite that can be consumed is proportional to the amount of water available, less water being required at higher temperatures due to increased solubility of sulphur (Connolly and Cesare 1993). At relatively low temperatures (and low S solubilities), extreme volumes of water are needed to completely consume all pyrite in a pyrite-rich rock, whereas at higher temperatures (and high S solubilities) only moderate volumes of water are needed. Secondly, massive sulphides commonly contain relatively small proportions of the hydrous minerals that release metamorphic water. Thus, externally derived fluids are required to advance the process.

When these sulphur-rich hydrothermal fluids migrate into the wall rocks they can react with iron-bearing minerals to form pyrrhotite, for example:

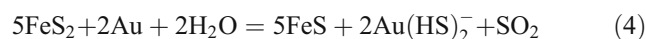


This process has been documented at several localities where pyrite-rich assemblages were metamorphosed at high temperatures and various metamorphic Fe-bearing minerals were affected (e.g. Tracy and Robinson 1988). At Montauban, this process is best represented where sulphur-rich fluids have interacted with adjacent amphibolites causing breakdown of hornblende to form pyrrhotite, tremolite (i.e. similar to reaction 3), anthophyllite/gedrite and phlogopite in varying proportions (Fig. 2a and b). This results in a characteristic alteration assemblage that expands the size of the exploration target. All Fe–Mg minerals, such as cordierite, amphibole, biotite and garnet, become Fe-depleted and some thus become pale coloured (biotite changes to phlogopite, hornblende to tremolite, anthophyllite/gedrite). Vectors towards ore can be generated through analysis of the Fe/Mg ratio of several of these minerals. Lower Fe/Mg ratios indicate increasing proximity to ore. Colour index of biotite, for example, could be used as a field proxy (more pale = increased proximity to

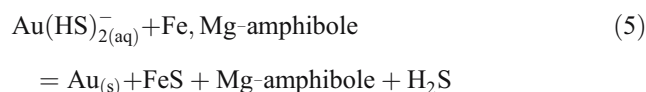
ore). Sulphidation has also been cited by many authors as an important mechanism of gold deposition in orogenic gold deposits (e.g. Neall and Phillips 1987; Hofstra et al. 1991). However, in most instances, the sulphur concentration in these regionally generated hydrothermal fluids is much lower, as is the metamorphic grade, and the alteration assemblages produced are consequently not as magnesian as those reported here (e.g. Neall and Phillips 1987). Externally derived, low sulphur hydrothermal fluids cannot produce the assemblage shown in Fig. 2, which has a high proportion of pyrrhotite and a small volume of highly magnesian silicates.

Note that this metamorphic alteration is different to alteration associated with the initial mineralisation event, which is developed within hydrothermal conduits formed beneath typical volcanogenic massive sulphide deposits. This initial alteration is also characterised, in some deposits, by low Fe/Mg ratios (Mg enrichment), but is typically (though not always) only developed stratigraphically below the mineralised horizon (e.g. Larson and Webber 1977; Franklin et al. 2005). In contrast, metamorphic alteration is not stratigraphically restricted. Metamorphism of an Mg-enriched, Fe-depleted initial alteration zone also produces cordierite–anthophyllite assemblages.

Pyrite de-sulphidation is capable of re-mobilising gold and other elements through reactions such as:



In a massive sulphide deposit such as Montauban, gold is transported away from the deposit because sulphur fugacity will remain high until the fluid encounters material capable of causing sulphur loss. At Montauban, this sulphidation process occurs within a short distance of the deposit when the H_2S -rich fluid encounters Fe-bearing wall rock. Gold precipitation therefore occurs through destabilisation of the gold bi-sulphide complex, for example:



This is not dissimilar to sulphidation reactions thought to be associated with gold deposition in orogenic gold deposits (e.g. Neal and Phillips 1987), except that here, both the S concentration in the fluid and the metamorphic grade are higher. Figure 2c shows that this process led to co-precipitation of pyrrhotite and gold (together with silver to form electrum) at Montauban. In effect, the massive sulphides are depleted in elements that easily form aqueous complexes with sulphur (i.e. Au and Ag, but not Pb and Zn), whereas the wall rocks are enriched in those elements. However, some gold is likely to escape the system because very high sulphur fugacity is required to drive reactions such as reaction 3, and therefore some sulphur-bearing fluid remains after equilibrium has been reached.

Bernier et al. (1987) noted that chalcopyrite is more abundant in the disseminated mineralisation of the gold zones than the massive sulphides. This is likely to partly reflect the pre-metamorphic distribution of metals, as Cu is precipitated in feeder zones of some VMS deposits together with Au and Ag (e.g. Franklin et al. 2005). However, Cu is also dissolved as $\text{Cu}(\text{HS})^{2-}$ (Mountain and Seward 2003), so some may have been transported from the massive sulphide bodies by the same mechanism described above.

This metamorphic alteration is distinguished from metamorphosed low Fe/Mg alteration that may have been associated with the initial mineralisation event by the observation (Fig. 2) that narrow alteration zones follow fractures that cut across the structural fabric. The alteration assemblage destroys the structural fabric. In the example, this occurs within an otherwise normal amphibolite with intermediate Fe/Mg hornblende compositions. Other regions within the disseminated mineralisation at Montauban contain wider zones of cordierite-anthophyllite-phlogopite rock with a well-developed structural fabric that may represent the metamorphosed equivalent of the initial alteration assemblage. Alternatively, it is possible that these zones represent an earlier generation of metamorphic alteration.

The process of metamorphic re-mobilisation and alteration described above occurs during prograde to syn-peak metamorphism and is distinct from retrograde hydrothermal re-mobilisation, which affects many deposits. Retrograde hydrothermal re-mobilisation results from addition of an externally derived fluid, and in many deposits this occurs under greenschist facies conditions. Such a low temperature fluid is not capable of carrying very high proportions of H_2S compared to those described above (ppm levels at greenschist facies conditions compared to several percent in the amphibolite facies; Connolly and Cesare 1993) and thus generates distinctly different hydrothermal alteration assemblages. Generally, all minerals other than quartz are partially or wholly altered to sericite, actinolite and chlorite, the Fe–Mg silicates are not extensively Fe-depleted, and the grain size is greatly reduced (Tomkins and Mavrogenes 2002). If any sulphide is precipitated under these lower temperature conditions, it is usually pyrite (see Fig. 2d). Gold may also be re-mobilised by this process, particularly if the fluid flux is high, because then more H_2S is able to interact with mineralisation. Retrograde hydrothermal re-mobilisation of gold at Montauban was not observed in this study, although it remains a possibility. Williams (1990b) found that gold at the similar Calumet Zn–Pb–Ag–Au deposit is associated with alteration ranging from pre-peak metamorphic timing to post-peak at greenschist facies conditions and interpreted that gold was externally derived; although it was acknowledged that gold could have been internally derived.

The alternative of gold addition by an external fluid during high temperature metamorphism at Montauban is considered unlikely. Addition of gold as a sulphide complex to an amphibolite facies rock that already contains sulphides would likely cause sulphidation of pyrrhotite to form pyrite, which is not observed. Further, at the metamorphic conditions indicated at Montauban, extreme $f\text{S}_2$ conditions are required to either drive sulphidation of pyrrhotite (Fig. 2d) or sulphidation of Fe–Mg silicates (cf. Tracy and Robinson 1988; Connolly and Cesare 1993). Such S-rich fluids are simply not found in regional metamorphic fluids and are only generated in the immediate vicinity of pyrite-rich occurrences (such as Montauban or Calumet) through reactions 1 and 2. This statement is made because reduced hydrothermal fluids can contain >20 mol% H_2S at 650°C and 6 kbar on the pyrite–pyrrhotite buffer (see Fig. 5d of Connolly and Cesare 1993), whereas regional metamorphic fluids associated with formation of orogenic gold deposits may contain on the order of 0.02 to 0.03 mol% H_2S (Neall and Phillips 1987).

Sulphide melting at Montauban

Observations

Previously, it was mentioned that the majority of disseminated sulphides in the north and south gold zones are situated at grain boundaries in equilibrium with the metamorphic fabric, and this is compatible with the observations by Bernier et al. (1987). Some sulphides also occur as inclusions within peak metamorphic amphibole and garnet. In many places there is no hydrothermal alteration associated with these modes of sulphide occurrence.

In some instances the disseminated sulphides are more concentrated within bands 2 mm to 4 cm thick. Figure 3 shows a selection of multi-mineral sulphide aggregations from within two of these more sulphide-rich bands, neither of which has hydrothermal alteration associated. It can be seen that the mineralogy of these bands is quite diverse. The list of minerals found in these bands includes (as determined by electron microprobe): galena, arsenopyrite, pyrrhotite, gudmundite (FeSbS), Au-bearing dyscrasite (Ag_3Sb , with gold contents up to 14.8 wt%), pyrrargyrite (Ag_3SbS_3), tetrahedrite ($(\text{Ag,Cu})_{10}(\text{Fe,Zn,Cu})_2(\text{Sb,As})_4\text{S}_{13}$), acanthite (Ag_2S), lollingite (FeAs_2), electrum, miargyrite (AgSbS_2), pyrite, geochronite ($\text{Pb}_{14}(\text{Sb,As})_6\text{S}_{23}$), twinnite (PbSb_2S_4), stephanite (Ag_5SbS_4), fizelyite ($\text{Pb}_{14}\text{Ag}_5\text{Sb}_{21}\text{S}_{48}$), bournonite (PbCuSbS_3), stannite ($\text{Cu}_2\text{FeSnS}_4$) and sphalerite, in approximate order of abundance. More dispersed disseminated pyrrhotite is found immediately outside these bands. The bulk compositions of some of these multi-mineral aggregations are given in Table 1, and plotted on Fig. 4.

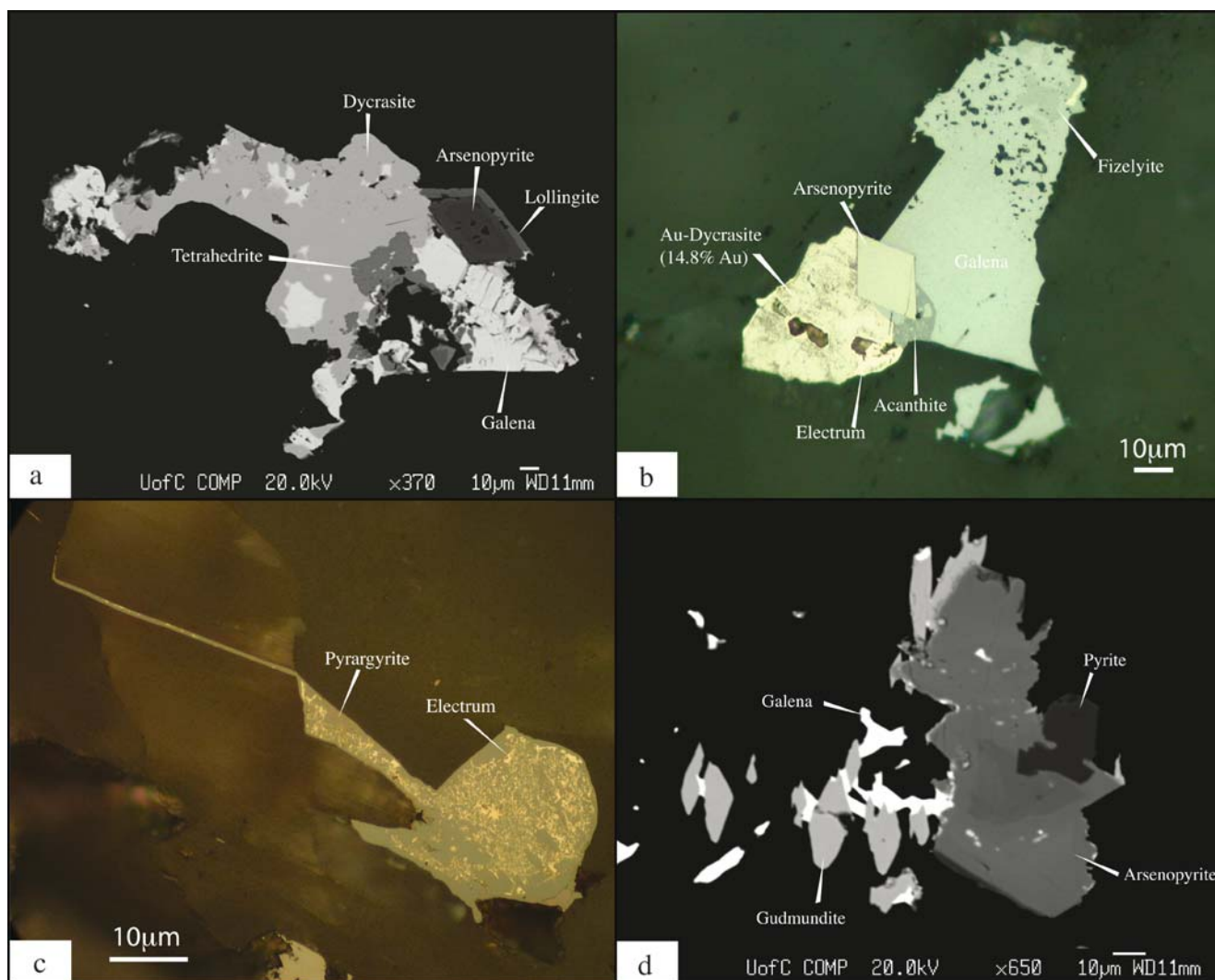


Fig. 3 Textures and mineral associations resulting from sulphide melt remobilisation at Montauban. **a** and **b** Minerals crystallised from stage 1 melt. **c** Pyrargyrite and electrum in part of a stage 2 sulphide melt

veinlet. **d** Arsenopyrite + pyrite after pyrrhotite, together with gudmundite and galena

It can be seen in Fig. 4 that when plotted to investigate galena and arsenopyrite fractionation, these data are positioned in nearly linear trends (correlation coefficients are shown). There is considerable error inherent in the technique used for measuring the bulk composition of these multi-mineral aggregations, which must overestimate the abundance of some phases and underestimate the abundance of others. However, if the data simply reflected variability in the way each multi mineral aggregate was cut, rather than fractionation, they would plot in a random scatter rather than the observed near-linear arrangement.

Discussion

Sulphide melting has previously been reported at Montauban (Tomkins et al. 2006, 2007) and these works are summarised and added to here. In massive Pb–Zn deposits, melting

first occurs through arsenopyrite breakdown under high f_{S_2} conditions generated by pyrite de-sulphidation. The As–S melt then consumes some galena, but there is typically more galena than can be completely melted, so some remains solid and the melt is then galena-saturated. This is the process that drove melting at Montauban.

Because sulphide melts have low viscosities, they partition strain easily and are consequently re-mobilised efficiently into dilational structures (Tomkins et al. 2004). Other elements are incorporated through mobilisation-assisted melting (Tomkins et al. 2007) at this stage. This process incorporates elements that preferentially partition into sulphide and sulphosalt melts, and at Montauban these included Sb, Ag and Au in particular, and minor Cu, Fe, Bi, Sn and Zn (in order of decreasing abundance). Based on observations at several deposits, it appears that Fe and Zn do not partition strongly into low-temperature sulphide or

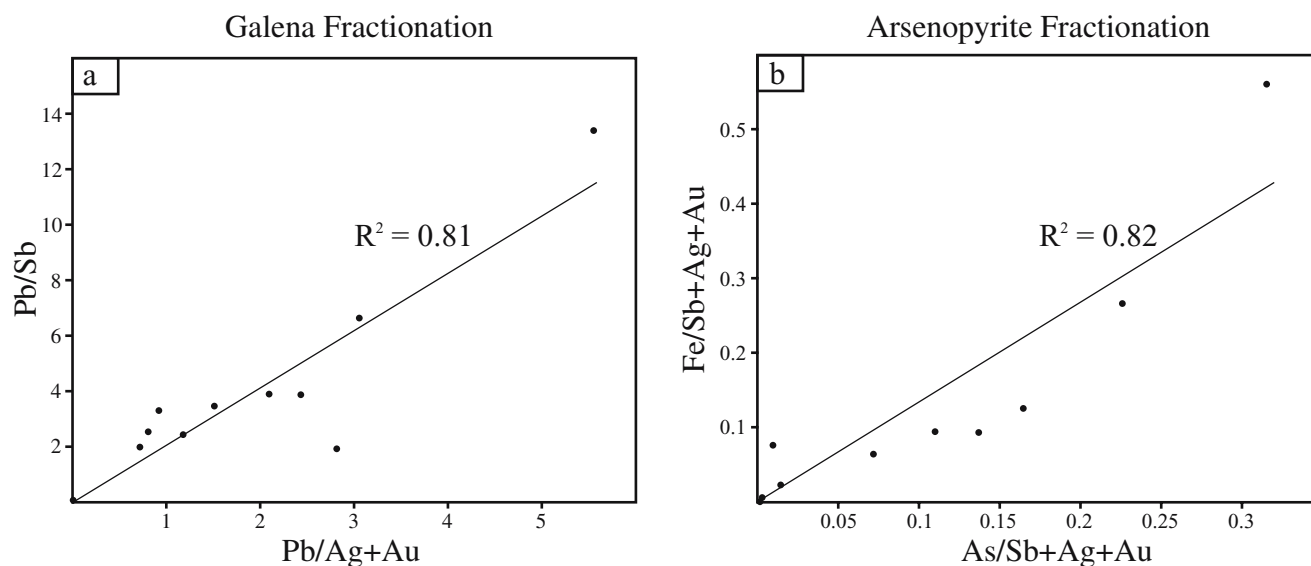


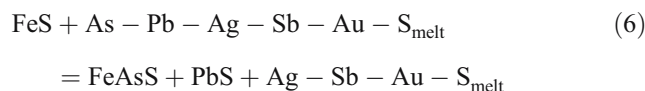
Fig. 4 Fractionation of the Pb–As–Sb–Ag–Au–S melt at Montauban. **a** Fractionation of through galena crystallisation. **b** Fractionation of through arsenopyrite crystallisation

sulphosalt melts (melts stable at amphibolite facies conditions), so segregation separates precious metal- and sulphosalt-rich material from Fe and Zn-rich restite.

Because of the limitations on sampling at Montauban, only two samples, from different drill holes, contained evidence for sulphide melting, and this may reflect the proportion of melt developed. This melt-derived material is distinguished from the hydrothermal re-mobilisation by the lack of the extensive hydrothermal alteration described in the previous section (and shown in Fig. 2b and c). In addition, the ore mineral assemblages are distinctly different as can be seen by comparing Fig. 2c with Fig. 3a,b and c. An experiment performed on one of these samples by Tomkins et al. (2007) showed that the ore minerals melted when subjected to the temperature and pressure estimated for peak metamorphism. Both of these samples contained textures that suggest there were two stages of melt re-mobilisation. The first stage separated galena- and arsenic-rich sulphide melt from the massive sulphides, generating small bands anomalously rich in galena, arsenopyrite, sulphosalts and precious metal alloys in the wall rock (Fig. 3a and b). The second stage of melt re-mobilisation is seen as microveinlets bleeding from the stage-1 bands (Fig. 3c). These microveinlets are dominated by pyrrhite (Ag_3SbS_3), which has a low melting point (485°C at 1 bar; Bryndzia and Kleppa 1988), and minor dyscrasite (Ag_3Sb) and electrum.

It is thought that stage 1 melts were re-mobilised from massive sulphides because melt fractionation trends (Fig. 4a) indicate that the melt was saturated in galena, this being less likely to occur amongst disseminated sulphides. Arsenic also fractionated from the melt at an early stage (Fig. 4b), and it is thought that this occurred when the

migrating melt reacted with pyrrhite that was already in the wall rock. This process is suggested by many examples of arsenopyrite and other sulphosalts rimming and replacing pyrrhite, and in some cases converting pyrrhite to pyrite (Fig. 3d). Such a reaction would drive fractionation and may have proceeded thus:



Similar textures of gudmundite (FeSbS) rimming and replacing pyrrhite are also observed, suggesting that Sb was also fractionated from the melt at a relatively early stage. These fractionation processes led to enrichment of the remaining melt, initially in Sb, but particularly in the precious metals and explains the progression to Stage 2 melts. There are no published phase relations for the entire Au–Ag–Sb–S system, so the eutectic temperature in this system is unknown. However, the predominance of pyrrhite suggests that the melt may have crystallised at temperatures of 485°C or lower (cf. Okamoto and Massalski 1986; Bryndzia and Kleppa 1988). In this way, gold remained mobile as the rocks cooled well after peak metamorphism.

Discussion—relative importance of the re-mobilisation mechanisms

At Montauban, mechanical re-mobilisation was the most important of the three transfer mechanisms for controlling

the distribution of the main commodity, namely, the massive Zn–Pb mineralisation. This finding is in accord with research on similarly metamorphosed massive sulphide deposits reported by many other authors (e.g. Vokes 1971; Friesen et al. 1982; Barnes 1987; Newberry et al. 1993; Marshall et al. 2000). In many of these deposits, as at Montauban, ore body thickening associated with mechanical re-mobilisation has resulted in economic upgrading of the ore. Metamorphic fluids were not effective in significantly re-mobilising Zn and Pb. This was in part due to the relatively small volume of fluid generated through metamorphic de-volatilisation of chlorite relative to the large volume of Pb and zinc sulphides (small volumes of fluid can only transport small amounts of metal). In addition, the metamorphic fluids, which in general tend to be low salinity, were sulphur-rich, and these metals dissolve as chloride complexes rather than sulphide complexes (e.g. Hemley et al. 1992). Sulphide melting was not extensive enough to significantly re-mobilise Zn and Pb, although a very small proportion of Pb was re-mobilised by this mechanism.

In contrast, the Au and Ag mineralisation at Montauban was most strongly affected by a combination of prograde hydrothermal re-mobilisation and partial melting of the ore assemblage, both of which drove migration of these elements into, and probably within, the wall rocks. These elements are soluble in hydrothermal fluids as sulphide complexes (e.g. Gammons and Barnes 1989; Loucks and Mavrogenes 1999) and are strongly partitioned into sulphide melts (e.g. Tomkins et al. 2004; Sparks and Mavrogenes 2005). Although there is likely to have been some disseminated precious metal mineralisation in the wall rocks before metamorphism, these two re-mobilisation mechanisms upgraded the ore in this region.

Internally driven prograde metamorphic hydrothermal re-mobilisation only becomes important as the metamorphic grade moves into the amphibolite facies and probably ceases once metamorphic fluid has been driven out of the system. Muscovite dehydration can proceed without silicate melting at low pressures in the upper amphibolite facies and represents the last stage when internally driven hydrothermal re-mobilisation is possible on the prograde metamorphic path. Externally derived hydrothermal fluid is also unlikely to be abundant in the upper amphibolite facies as it promotes melting in metasedimentary rocks, which causes H₂O loss to the melt.

Metamorphic sulphide melting in massive Zn–Pb deposits starts in the middle amphibolite facies and becomes increasingly important as the temperature increases. During the initial stages of melting the proportion of melt is likely to be very low, but in the granulite facies, enough melt to form laterally extensive sulphide magma dykes can develop (Tomkins et al. 2007).

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