Relationship between CO$_2$-dominated fluids, hydrothermal alterations and gold mineralization in the Red Lake greenstone belt, Canada

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ABSTRACT

The Red Lake greenstone belt is one of the foremost Au mining camps in Canada and hosts the world-class Campbell-Red Lake Au deposit. Belt-scale hydrothermal alteration is characterized by proximal ferroan dolomite zones associated with Au mineralization surrounded by distal calcite zones, both being accompanied by potassic alterations (sericite, muscovite, and biotite). At the Campbell-Red Lake and Cochenour deposits Au mineralization (in particular high-grade ore) is associated with silica and sulfides (especially arsenopyrite) that replace carbonate ± quartz veins and the host rocks. The prevalence of carbonic fluid inclusions and rare occurrence of aqueous-bearing inclusions in carbonate–quartz–Au veins in the Campbell-Red Lake deposit, and the consistency of homogenization temperatures of carbonic inclusions within individual fluid inclusion assemblages (FIA), have been interpreted to indicate that H$_2$O-poor, CO$_2$-dominated fluids were responsible for the carbonate veining and Au mineralization. Further studies of fluid inclusions in carbonate–quartz veins within and outside the deformation zone hosting the Campbell-Red Lake deposit (the Red Lake Mine trend) including the Cochenour Au deposit, the Redcon Au prospect, and outcrops in the distal calcite zone also reveal the dominance of carbonic fluid inclusions in vein minerals. These studies indicate that CO$_2$-dominated fluids were flowing through fractures during carbonate vein formation and Au mineralization both within and outside major structures. The carbonic fluid may have been initially undersaturated with water, or it may have resulted from phase separation of an H$_2$O–CO$_2$–NaCl fluid. In the latter case, phase separation modeling indicates that the initial fluid likely had X$_{CO2}$ values larger than 0.8. Calculations based on hydrothermal mineral assemblages indicate X$_{CO2}$ values in the host rocks from 0.025 to 0.85, reflecting a change from CO$_2$-dominated fluids in the fractures (veins) to H$_2$O-dominated fluids in the host rocks away from the fractures. The CO$_2$-dominated fluids were likely advected from granulite facies in the deeper crust, whereas the H$_2$O-dominated fluids were derived from the ambient host rocks of amphibole to greenschist facies. Calculations based on CO$_2$ requirements and source constraints indicate that the mineralizing fluids were likely two orders of magnitude more enriched in Au than the commonly assumed values of a few µg/L, which may explain why the Campbell-Red Lake deposit has a very high-grade of Au (average 21 g/t for the whole deposit and 81 g/t for the Goldcorp High-Grade zone). Fluid inclusion data suggest that the carbonate veining and Au mineralization likely took place at depths from 7 to 14 km. The development of crustiform–colloform structures in the carbonate ± quartz veins, which was previously interpreted to indicate relatively shallow environments, may alternatively have been related to extremely high fluid pressures and the CO$_2$-dominated nature of the fluids, which could have enhanced the brittle properties of the rocks due to their high wetting angles.

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1. Introduction

It is well known that Au deposits formed in metamorphic terranes (Groves et al., 2003; Goldfarb et al., 2005), including orogenic Au deposits (Groves et al., 1998) or greenstone-hosted quartz–carbonate vein-type Au deposits (Poulsen et al., 2000; Dubé and Gosselin, 2007), and intrusion-related Au deposits (Lang and Baker, 2001), are commonly associated with CO$_2$-enriched, low-salinity fluids as recorded by fluid inclusions (Ridley and Diamond, 2000; Baker, 2002). According to Ridley and Diamond (2000), the CO$_2$ mole fraction of the ore-forming fluids ranges from 0.05 to 0.90, but the most frequently recorded values are in the range from 0.10 to 0.25, indicating H$_2$O-dominated fluid systems. However, in some deposits, including the world-class Ashanti Au belt (Ghana) and Campbell-Red Lake Au deposit (Canada), fluid inclusion studies suggest that the ore-forming fluids were dominated by CO$_2$ (Schmidt Mumm et al., 1997, 1998; Chi et al., 2006). In these...
and a few other examples, e.g., the Bin Yauri Au deposit in Nigeria (Garba and Akande, 1992) and the Fazenda Maria Preta Au deposit in Brazil (Xavier and Foster, 1999), carbonic fluid inclusions without a visible aqueous phase are almost the only type of inclusions present. Although carbonic inclusions may be produced by fluid phase separation (e.g., Robert and Kelly, 1987; Guha et al., 1991) and/or preferential leakage of H2O relative to the carbonic components after entrapment (Hollister, 1988, 1990; Bakker and Jansen, 1994; Johnson and Hollister, 1995), these mechanisms cannot satisfactorily explain why so few aqueous inclusions were entrapped and/or preserved in these cases, and so the predominance of carbonic fluid inclusions is interpreted to reflect a CO2-dominated fluid system (Schmidt Mumm et al., 1997, 1998; Chi et al., 2006). It remains unclear, however, how such fluids originated and were distributed in the greenstone belts, and how they are related to Au mineralization and hydrothermal alteration including hydrous mineral assemblages (Klemd, 1998; Ridley and Diamond, 2000; Goldfarb et al., 2005). These questions are examined in this paper for the Archean Red Lake greenstone belt, Canada, where the predominance of carbonic fluid inclusions has been reported for the Campbell-Red Lake deposit (Tarnocai, 2000; Chi et al., 2002, 2003, 2006).

The Red Lake greenstone belt in western Ontario is one of Canada’s foremost Au mining districts, with 105 Au showings/deposits within a small area of about 500 km² (Fig. 1; Sanborn-Barrie et al., 2004). The total production plus remaining reserve and resources is nearly 1000 t of Au, of which 840 t is from the Campbell-Red Lake Au deposit (Chi et al., 2006, in written communication from S. McGibbon in 2005) and about 150 t from the remaining deposits (Lichtblau and Storey, 2005). The Campbell-Red Lake deposit has been interpreted as a metamorphosed epithermal deposit (Penczak and Mason, 1997, 1999), but several other studies (e.g., MacGeehan et al., 1982; Mathieson and Hodgson, 1984; Andrews et al., 1986; Tarnocai et al., 1997; Menard and Pattison, 1998; Tarnocai, 2000; Parker, 2000; Thompson, 2003; Dubé et al., 2004) indicate a broadly contemporaneous relationship between the mineralization, regional deformation, magmatic intrusion and metamorphism (i.e., syn-orogeny). Also the geological setting as well as structural and alteration features shares similarities to those of orogenic Au deposits (Groves et al., 1998). However, unlike most greenstone-hosted orogenic Au deposits where carbonate contents in the veins are less than 5–15 vol.% (Goldfarb et al., 2005), carbonate constitutes the original main components of Au-bearing carbonate ± quartz veins in the Campbell-Red Lake Au deposit. The abundance of carbonate alteration throughout the greenstone belt, and the unusually well developed carbonate ± quartz veins with which Au mineralization is commonly associated spatially, have been noticed by many authors (e.g., Andrews et al., 1986; Parker, 2000; Poulsen et al., 2000; Dubé et al., 2003), but the relationship between the carbonate alteration/veining and the newly recognized CO2-dominated fluids (Chi et al., 2006), and the apparent conflict between the development of hydrous alteration and the H2O-poor nature of the CO2-dominated fluids, has never been examined.

This paper summarizes the evidence for CO2-dominated fluids in the Campbell-Red Lake Au deposit (Tarnocai, 2000; Chi et al., 2006).
rocks were metamorphosed to greenschist-to-amphibole facies (2704–2699 Ma).

2. Geological setting

The Red Lake greenstone belt is part of the Uchi subprovince of the Superior province. It consists of Mesoarchean (2990–2890 Ma) and Neoarchean (2750–2730 Ma) volcanic-dominated rocks (Sanborn-Barrie et al., 2004 and references therein). The Mesoarchean comprises mafic-ultramafic volcanic rocks of the Balmer assemblage (2990–2960 Ma), intermediate to felsic calc-alkaline flows (2940–2920 Ma), and intermediate calc-alkaline pyroclastic rocks overlain by clastic sedimentary rocks and banded iron-formation of the Bruce Channel assemblage (Dubé et al., 2004; Sanborn-Barrie et al., 2004 and references therein). The Neoarchean rocks, separated by a regional unconformity from the Mesoarchean, consist of calc-alkaline and tholeiitic volcanic and volcaniclastic rocks of the Confederation assemblage (2750–2730 Ma), polymeric conglomerate and finer clastic sedimentary rocks of the Huston assemblage, and calc-alkaline rocks of the Graves assemblage (ca. 2732 Ma) (Dubé et al., 2004; Sanborn-Barrie et al., 2004 and references therein).

The supracrustal assemblages were affected by two main episodes of penetrative deformation: D1 is related to a W–E shortening stress regime from ca. 2742 to 2733 Ma, whereas D2 reflects N–S shortening related to the Uchian phase of the Kenoran orogeny between ca. 2723 and 2712 Ma, which is related to the collision between the North Caribou terrane to the north of the Red Lake greenstone belt and the Winnipeg River terrane to the south (Sanborn-Barrie et al., 2004). More recently, Percival et al. (2006) indicated that this large scale collisional event (Uchian orogeny) occurred from ~2.72 to 2.70 Ga. Post-collisional deformation (D3) is locally recorded and its age is constrained to be after ca. 2700 Ma (Menard et al., 1999; Dubé et al., 2004).

The supracrustal rocks were intruded by granitoid s of various ages (Fig. 1), including the Douglas Lake pluton (2734 Ma), Little Vermilion Lake batholith (2731 Ma), Hammell Lake pluton (2717 Ma), Dome stock (2718 Ma), Killala-Baird batholith (2704 Ma), and Cat Island pluton (2697–2699 Ma) (Corfu and Andrews, 1987; Dubé et al., 2004; Sanborn-Barrie et al., 2004). Felsic-intermediate dykes of 2714–2696 Ma and lamprophyre dykes of 2702–2699 Ma are present (Dubé et al., 2004). The granitoids are classified by Thompson (2003) into 3 groups: (1) pre-orogenic (>2730 Ma), (2) early syn-orogenic (2720–2717 Ma), and (3) late syn-orogenic (2704–2699 Ma).

The volcanic and sedimentary rocks and the early granitoid rocks were metamorphosed to greenschist-to-amphibole facies (Sanborn-Barrie et al., 2004, and references therein). Metamorphic grade increases from greenschist facies in the middle of the greenstone belt to amphibole facies at the margin of the belt, which is surrounded by granitoid intrusions, and the boundaries between metamorphic zones (isograds) are broadly parallel to the contact between the supracrustal rocks and the granitoid rocks (Andrews et al., 1986; Damer, 1997; Thompson, 2003). This metamorphic pattern has been interpreted by many (Andrews et al., 1986; Damer, 1997; Menard and Pattison, 1998; Tarnocai, 2000) as indicating contact metamorphism. However, Thompson (2003) pointed out that some of the granitoid intrusions are too young or too old to be the heat source for regional metamorphism, which peaked during the major phase of the orogeny, and petrographic evidence indicates that the main phase of metamorphism overlapped with ductile deformation associated with crustal shortening and thickening. Therefore, although granitoid intrusions likely caused localized contact metamorphism, which overprinted regional metamorphism, the metamorphic pattern of the Red Lake greenstone belt mainly reflects the results of peak regional metamorphism during D2 (Thompson, 2003). In other words, both granitoids and regional metamorphism are products of crustal shortening and thickening, with granitoid intrusions outlasting peak metamorphism.

Gold deposits, mostly hosted in the Balmer assemblage, occur along major deformation zones (Andrews et al., 1986) and are commonly spatially associated with carbonate ± quartz veins. However, besides the Campbell-Red Lake and Cochenour Au deposits, there are other styles of Au mineralization in Red Lake as illustrated by the amphibolite-facies, disseminated-replacement-style Au mineralization at Madsen, the second largest deposit in the district (Dubé et al., 2000) or the carbonate–tourmaline Au-bearing veins as typified by the Buffalo mine. The Campbell-Red Lake deposit, by far the largest deposit in the district, is characterized by numerous barren to low grade colloform–crustiform, cavity-filling carbonate ± quartz veins overprinted by auriferous silicification (MacGeehan and Hodgson, 1982; Penczak and Mason, 1997, 1999; Tarnocai, 2000; Twomey and McGibbon, 2001; Dubé et al., 2001, 2002, 2004). As indicated in Dubé et al. (2004), five different styles of Au mineralization are present in the Campbell-Red Lake deposit: (1) sulfide-rich veins and replacement-style ore, mainly present at the Red Lake mine and spatially associated with the Dickinson and the Campbell faults, (2) carbonate ± quartz veins, better developed in the upper portion of the deposit at the Campbell mine, (3) magnetite-rich ore, (4) high-grade arsenopyrite-rich silicification characterized by multi-ounce ore zones that typify the Goldcorp High-Grade zone, and (5) abundant visible Au coating and filling late fractures. The Goldcorp High-Grade zone of the Campbell-Red lake deposit is the best example of styles 3, 4 and 5 (Dubé et al., 2004). The timing of Au mineralization has been controversial. The colloform–crustiform and cockade structures that are well developed in the carbonate ± quartz veins led Penczak and Mason (1997, 1999) to interpret the carbonate veining and mineralization as pre-penetrative deformation and pre-regional metamorphism events, and assigned the Campbell-Red Lake Au deposit to a deformed and metamorphosed low-sulfidation epithermal type. Several authors (e.g., MacGeehan et al., 1982; Mathieson and Hodgson, 1984; Andrews et al., 1986; Tarnocai et al., 1997; Menard and Pattison, 1998; Tarnocai, 2000; Parker, 2000; Twomey and McGibbon, 2001; Thompson, 2003; Dubé et al., 2004), however, consider Au mineralization as broadly syn-deformation and syn-metamorphic, although the interpretation of the age(s) of peak metamorphism is different for different authors. Based on their study of the Goldcorp High-Grade zone at the Red Lake mine of the Campbell-Red lake deposit, Dubé et al. (2004) constrained the age of the high-grade Au mineralization to be mainly between 2723 and 2712 Ma, an interval similar to...
those proposed by Corfu and Andrews (1987) and Penczak and Mason (1997) for the entire Campbell-Red Lake deposit. This age interval is also in the same range as the main phase metamorphism and deformation defined by Thompson (2003), and broadly coincides with the Uchian orogeny (Sanborn-Barrie et al., 2004; Percival et al., 2006). Minor mineralization took place after 2702 Ma, probably related to D3 (Menard et al., 1999; Dubé et al., 2004).

The Red Lake greenstone belt has experienced extensive hydrothermal alteration, most noticeably carbonate alteration. Parker (2000) divided carbonate alteration into two types, i.e., “proximal ferroan dolomite alteration”, where major Au deposits occur, and “distal calcite alteration”, where only minor Au occurrences are found (Fig. 1). Conflicting crosscutting relationships between calcite and ferroan dolomite veins in the boundary zone between the two types of carbonate alteration suggests that they are broadly contemporaneous (Parker, 2000). Besides carbonatization, potassic alteration is also widespread in the Red Lake greenstone belt (Andrews et al., 1986; Parker, 2000). The potassic alteration in the distal calcite zones is characterized by sericitization, whereas in the proximal ferroan dolomite zones consists of sericite/muscovite/fuchsite and some biotite in the greenschist facies, and pervasive biotite + muscovite in amphibolite-facies (Parker, 2000). At the vein or replacement ore scale in the Goldcorp High-Grade zone of the Red Lake mine, Au-bearing silicified carbonate ± quartz veins are commonly surrounded by a centimeter- to meter-wide reddish-brown biotite–carbonate alteration envelope, and by an outer, meter-wide, garnet–chlorite–magnetite assemblage (Damer, 1997; Twomey and McGibbon, 2001; Dubé et al., 2004; Cadieux et al., 2006, and references therein) locally associated with centimeter- to meter-wide barren “bleached zone” containing andalusite-muscovite-quartz-ilmenite in the amphibolite facies domains (Tarnocai, 2000; Twomey and McGibbon, 2001; Dubé et al., 2002, 2004; Cadieux et al., 2006). In the Campbell-Red Lake deposit, the aluminous bleached zones are common in variolitic pillowed flows and represent an early pre-mineralization assemblage (Penczak and Mason, 1999; Tarnocai, 2000; Dubé et al., 2004; Cadieux et al., 2006). Cadieux et al. (2006) indicated that in the Goldcorp High-Grade zone the aluminous assemblage is pre-colloform carbonate ± quartz veins and has no clear spatial relationship with the high-grade ore. Such aluminous alteration is compatible with metamorphosed argillic and advanced argillic alteration due to acid leaching by low pH fluids (Penczak and Mason, 1997; Cadieux et al., 2006). In the Goldcorp High-Grade zone, Au mineralization is clearly related to silica and arsenopyrite replacement of carbonate ± quartz veins and the host rocks (Dubé et al., 2002, 2004), but reddish-brown biotite–carbonate alteration is also considered to be related at least spatially to the auriferous hydrothermal system (Twomey and McGibbon, 2001; Dubé et al., 2002, 2004). However, biotite–carbonate alteration is also found where there is no silica-arsenopyrite replacement and Au mineralization (Cadieux et al., 2006), and auriferous silica and arsenopyrite alteration is seen replacing biotite–carbonate alteration (Dubé et al., 2002; Parker, 2000). Biotitic alteration in amphibolite-facies metavolcanic rocks may also contain variable amounts of aluminosilicate minerals such as andalusite, staurolite and cordierite, which have been interpreted to have formed from metamorphism of previously altered rocks (Penczak and Mason, 1999; Parker, 2000).

3. CO2-dominated fluid inclusions in the Red Lake greenstone belt

The development of extensive carbonate alteration in the Red Lake greenstone belt, as outlined above, does not necessarily indicate involvement of CO2-dominated fluids. The evidence for CO2-dominated fluids comes mainly from fluid inclusions entrapped in hydrothermal vein minerals, particularly the predominance of carbonic fluid inclusions without a visible aqueous phase and the rarity of aqueous inclusions, as observed in the Campbell-Red Lake deposit (Chi et al., 2003, 2006). Similar observations are made in this study for three other occurrences (Cochenour, Redcon, and Sandy Bay – Woodland Cemetery outcrops) with different local geological setting in the eastern part of the Red Lake greenstone belt (Fig. 1). These observations are summarized in Table 1 and described below. Fluid inclusions randomly distributed in three dimensions and occurring in isolation and clusters are interpreted as primary or pseudosecondary inclusions. All the fluid inclusions studied are considered to be primary or pseudosecondary unless otherwise indicated (labelled “s” in Table 1).

The Campbell-Red Lake Au deposit is located in a SE-trending hydrothermal/structural corridor known as the Red Lake Mine trend (Dubé et al., 2003, 2004, and references therein). The deposit, located within the proximal ferroan dolomite alteration zone of Parker (2000), is characterized by numerous barren to low-grade banded crustiform ankerite ± quartz veins and ankerite-cemented cockade breccias, which are replaced and overprinted by quartz and associated sulfides (mainly arsenopyrite) and native Au. In the Goldcorp High-Grade zone, the Au-bearing silicified carbonate ± quartz veins are commonly surrounded by a biotite–carbonate alteration envelope (Fig. 2A) (Twomey and McGibbon, 2001; Dubé et al., 2004; Cadieux et al., 2006, and references therein). The host rocks were metamorphosed to greenschist–amphibole facies (transition zone) (Thompson, 2003). Fluid inclusions in ankerite and associated quartz (Q1) as well as in quartz associated with Au (Q2) are predominantly carbonic, while aqueous and aqueous-carbonic inclusions are rare, and bulk analysis of fluid inclusions by gas chromatography indicates negligible H2O (Chi et al., 2006). However, aqueous and aqueous-carbonic inclusions are common in post-mineralization calcite and quartz (Q3) (Chi et al., 2003). The aqueous inclusions studied in Q1, Q2, and Q3 are isolated, scattered and clustered, and are considered as primary and pseudosecondary as are carbonic inclusions, although the co-entrapment of carbonic inclusions and aqueous inclusions has not been shown by fluid inclusion assemblages (Chi et al., 2002, 2003, 2006). Homogenization temperatures of carbonic inclusions range from −2.4 to +30.6 °C (to liquid) for ankerite and +0.3 to +26.5 °C for Au-related quartz (Table 1). Despite these overall wide ranges, homogenization temperatures within individual fluid inclusion assemblages (FIA) are consistent, arguing against post-entrapment modification (preferential H2O leakage) as the mechanism of formation of carbonic inclusions (Chi et al., 2006). Homogenization temperatures of aqueous inclusions range from 171 to 344 °C, 252–380 °C, and 73–326 °C for ankerite, auriferous quartz and post-ore quartz and calcite, respectively (Table 1).

The Cochenour Au deposit is hosted by the same deformation zone as the Campbell-Red Lake deposit (i.e., the Red Lake Mine trend) and located within the greenschist–amphibole transition zone (Thompson, 2003) and the proximal ferroan dolomite alteration zone (Parker, 2000). It is characterized by extensive carbonate ± quartz veinings (Fig. 2B) overprinted, at least in part, by silicification, sulfide replacement, and Au mineralization (Dubé et al., 2003, and references therein). Fluid inclusions are predominantly carbonic in ankerite and associated coarsely crystalline quartz (Q1) and in Au-associated fine-grained quartz (Q2). Aqueous and aqueous-carbonic inclusions are generally rare, but can be locally common in some of the quartz associated with ankerite (Q1). Homogenization temperatures of carbonic inclusions range from −12.6 to +20.5 °C (to liquid) for ankerite and −0.2 to +20.5 °C for Au-related quartz (Table 1). Homogenization temperatures of aqueous inclusions in quartz associated with ankerite range from 110 to 265 °C (Table 1).
The Redcon Au prospect is situated about 4 km NE of the Red Lake Mine trend, in an area of relatively weak deformation. It is located within the transition zone between greenschist and amphibole facies (Thompson, 2003) and the proximal ferroan dolomite alteration zone (Parker, 2000). A 1–2 m wide ankerite vein cuts weak foliations, and is in turn cut by quartz-actinolite stringers associated with Au (Fig. 2C). Fluid inclusions in ankerite and quartz (Q2) are predominantly carbonic, with homogenization temperatures ranging from +2.0 to +26.5 °C and from +25.0 to +31.0 °C (to liquid), respectively (Table 1). Homogenization temperatures of isolated carbonic inclusions are similar within individual quartz grains (Fig. 3A), and fall in a very small range within individual healed fractures (Fig. 3B), supporting a non-H2O leakage origin of the carbonic inclusions. Aqueous and aqueous-carbonic inclusions are common in healed fractures, likely of secondary origin, and have homogenization temperatures from 235 to >255 °C (Table 1).

The outcrops near the intersections of the Sandy Bay and Woodland Cemetery roads with Highway 125 are situated less than 3 km south of the Red Lake Mine trend. The host rocks are within the greenschist facies (Thompson, 2003) and the distal calcite alteration zone (Parker, 2000). Centimeter-scale calcite-quartz veins occur in relatively low-strained volcanic rocks (Fig. 2D). Fluid inclusions are generally less developed than in other occurrences. Carbonic inclusions are abundant in quartz associated with calcite.

### Table 1: Characteristics of fluid inclusions from four different deposits/occurrences in eastern Red Lake greenstone belt.

<table>
<thead>
<tr>
<th>Localities</th>
<th>Campbell-Red Lake deposit</th>
<th>Cochenour deposit</th>
<th>Redcon prospect</th>
<th>Sandy Bay–Woodland Cemetery</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Deformation zone</strong></td>
<td>Red Lake Mine trend</td>
<td>Red Lake Mine trend</td>
<td>Low-strain zone</td>
<td>Low-strain zone</td>
</tr>
<tr>
<td><strong>Metamorphic grade</strong></td>
<td>Greenschist–amphibole transition</td>
<td>Greenschist–amphibole transition</td>
<td>Greenschist–amphibole transition</td>
<td>Greenschist</td>
</tr>
<tr>
<td><strong>Alteration zone</strong></td>
<td>Proximal ankerite Ank – Q1</td>
<td>Proximal ankerite Ank – Q1</td>
<td>Proximal ankerite Ank – Q1</td>
<td>Distal calcite Cal3-Q3</td>
</tr>
<tr>
<td><strong>Host mineral</strong></td>
<td>Q2 (syn-ore) Cal3-Q3</td>
<td>Q2 (syn-ore) Cal3-Q3</td>
<td>Q2 (syn-ore) Cal3-Q3</td>
<td>Q2 (syn-ore) Cal3-Q3</td>
</tr>
<tr>
<td><strong>Carb FI</strong></td>
<td>++++</td>
<td>++++</td>
<td>++++</td>
<td>++++</td>
</tr>
<tr>
<td>Aq-Carb FI</td>
<td></td>
<td></td>
<td>–</td>
<td>++ (s)</td>
</tr>
<tr>
<td>T°a of Carb FI</td>
<td>–2.4 to +30.6 (L)</td>
<td>+0.3 to +26.5 (L)</td>
<td>12.6 to +20.5 (L)</td>
<td>+2.0 to +26.5 (L)</td>
</tr>
<tr>
<td>T°a of Aq FI</td>
<td>171–344 (L)</td>
<td>252–380 (L)</td>
<td>110–265 (L)</td>
<td>235 to &gt;255 (L)</td>
</tr>
</tbody>
</table>

Carb = carbonic; FI = fluid inclusions; Aq = aqueous; T°a = homogenization temperatures [°C]; Ank = ankerite; Q1 = quartz associated with ankerite; Q2 = quartz post-dating ankerite and associated with gold mineralization; Cal 3 = calcite (post-mineralization); Q3 = quartz post-dating mineralization and associated with calcite; Q-D = quartz (distal zone); ++++ = predominant; +++ = abundant; + = common; – = rare; (s) = common as secondary inclusions.

Data for the Campbell-Red Lake deposit are from Chi et al. (2002, 2003, 2006); others are from this study.

Fig. 2. Photographs showing the occurrences of carbonate–quartz veins in different localities in eastern Red Lake greenstone belt: (A) a crustiform ankerite vein with silicification and Au mineralization, surrounded by a biotite–carbonate alteration envelope, from the Red Lake mine; (B) an ankerite vein with crustiform structures cut by minor quartz veinlets, Cochenour deposit; (C) an ankerite vein (rusted) crosscut by minor quartz veinlets (white), Redcon prospect; (D) calcite–quartz veins in the distal calcite zone, outcrop near the intersection of the Sandy Bay Road and Highway 125.
In summary, carbonic inclusions without a visible aqueous phase are predominant in the Campbell-Red Lake and Cochenour deposits and Redcon prospect and abundant in the Sandy Bay – Woodland Cemetery outcrops. The absence of an aqueous phase, even in relatively large and angular carbonic inclusions, together with gas chromatography analyses of bulk fluid inclusions from the Campbell-Red Lake deposit which indicate negligible H₂O (Chi et al., 2006), suggests that the carbonic inclusions are truly very low in water. The fact that the homogenization temperatures of the carbonic inclusions fall in a small range within individual fluid inclusion assemblages indicates that the carbonic inclusions did not result from preferential leakage of H₂O from initially carbonic-aqueous inclusions – such a mechanism would likely have caused different degrees of H₂O leakage depending on the size and shape of individual inclusions, leading to coexistence of fluid inclusions of different CO₂/H₂O ratios and different homogenization temperatures. As shown in the next section, the carbonic inclusions may have been produced by phase separation of an initially carbonic-aqueous fluid, but this initial fluid must be CO₂-dominated as constrained from phase separation modeling. Therefore, the fluid inclusion data indicate that CO₂-dominated fluids were circulating in the fracture systems in the Red Lake greenstone belt during carbonate veining and Au mineralization. These fluids were not only active within major deformation zones (the Red Lake Mine trend), but were present in the less strained areas as well (e.g., the Redcon prospect and Sandy Bay – Woodland Cemetery outcrops). The CO₂-dominated fluids were not limited to the proximal ankerite zone hosting major Au mineralization either, but were also present in the distal calcite zones. However, aqueous components became more important after the main phase of carbonatization and Au mineralization, as reflected by the common occurrences of primary aqueous inclusions in post-mineralization quartz and calcite and secondary aqueous inclusions in other vein minerals.

### 4. P-T conditions and constraints on X_{CO₂} from fluid phase separation modeling

The limited number of aqueous inclusions from the Campbell-Red Lake deposit gives a large range of homogenization temperatures from 171 to 380 °C (Table 1), which are significantly lower than the peak metamorphism temperature (about 450–550 °C) estimated by different authors based on metamorphic mineral assemblages (Table 2). The main phase of Au mineralization in the Red Lake greenstone belt has been limited by isotopic dating to 2723–2712 Ma (Corfu and Andrews, 1987; Penczak and Mason, 1997; Dubé et al., 2004), which coincides with the main phase of regional metamorphism (Thompson, 2003). Textural evidence suggests that auriferous hydrothermal alteration was broadly synchronous with the peak metamorphism at the Campbell mine (Tarnocai et al., 1997; Tarnocai, 2000). The fact that hydrothermal alteration mineral assemblages change systematically with metamorphic grades (Parker, 2000) also suggests that the hydrothermal activities associated with Au mineralization in the Red Lake greenstone belt were broadly contemporaneous with regional peak metamorphism, similar to many orogenic Au deposits (Mikucki and Ridley, 1993; McCuaig and Kerrich, 1998). The reason why the homogenization temperatures of aqueous inclusions are so variable and lower than the peak metamorphism temperatures may be related to pressure fluctuation and physical separation of the aqueous and carbonic phases during trapping of the inclusions (Robert and Kelly, 1987). If an aqueous phase is saturated with the carbonic phase (i.e., the two phases are in physical contact with...
each other) during trapping of the inclusions, the homogenization temperatures should be equal to the trapping temperatures. However, if the two phases are physically separated (e.g., located in separate intracrystal microfractures), a decrease of fluid pressure will purge part of the carbonic component from the aqueous phase, and a later increase of fluid pressure will make the aqueous phase become undersaturated with the carbonic components (Robert and Kelly, 1987). If this aqueous phase is then entrapped (sealed) as inclusions, their homogenization temperatures will be lower than the trapping temperatures, and “pressure corrections” are required to obtain the trapping temperatures. Robert and Kelly (1987) have shown that temperature corrections ranging from 50 to 200 °C may be applicable to the aqueous inclusions in the case of the Sigma Au deposit in the Abitibi greenstone belt. Therefore, depending on the magnitude of fluid pressure fluctuation, the homogenization temperatures can be variably lower than the trapping temperatures, although it is possible that the higher part of the homogenization temperature spectrum may overlap with the trapping temperatures.

Taking into account all these considerations, it is proposed that the thermal conditions of mineralization of the Campbell-Red Lake deposit may be broadly limited in the range from 350 to 550 °C. Using this temperature range and the isochore derived from the lower limit of homogenization temperatures of carbonic inclusions (~2.4 °C), the fluid pressures are estimated to be 2.7–3.6 kbar (Table 2). These pressures are comparable to those estimated from metamorphic mineral assemblages, i.e., 3.8–4.2 kbar estimated by Mathieson and Hodgson (1984), 3–4 kbar by Christie (1986), and <3 kbar by Tarnocai (2000), but are significantly higher than the 1.0–2.2 kbar estimated by Damer (1997). Thompson (2003) noted that the pressure estimation by Damer (1997) is too low from the regional geologic setting consideration and proposed a possible range of pressure from 2 to 4 kbar.

Although it has been shown that the carbonic inclusions in the Red Lake greenstone belt are real records of fluids present during carbonate veining and Au mineralization, it remains a possibility that the carbonic inclusions represent the carbonate phase resulting from phase separation of an initially carbonic-aqueous fluid. The occurrence of aqueous inclusions (although rare) in the vein minerals together with carbonic inclusions is compatible with such a scenario. The question is what kind of composition is required of the initial fluid, given the temperature and pressure conditions discussed above, in order to produce an H2O-poor, carbonic fluid. To answer this question, a fluid phase separation modeling, using the UCSD-Chemical Geology Group “GeoFluids” program, which is based on the Duan et al. (1995) equation of state for the H2O–CO2–NaCl system, is carried out as follows.

The initial fluid is approximated by the H2O–CO2–NaCl system, and four different initial compositions are tested, with the mole fractions of H2O, CO2, and NaCl from 0.9 to 0.16, 0.07–0.80, and 0.03–0.04, respectively (Fig. 4). The NaCl composition is based on the most frequently recorded values in orogenic Au deposits (Ridley and Diamond, 2000; Fig. 4). Calculations were run for pressures of 2 and 3 kbar and temperatures of 400 and 500 °C to simulate the mineralization conditions, and tests were also made at lower pressure and temperature conditions (1 kbar and 300 °C) for comparison. For each initial composition, it is first tested whether or not phase separation can take place at the given pressure-temperature conditions. If there is phase separation, the vol.% density, and H2O–CO2–NaCl composition of the coexisting liquid and vapor phases at the time of entrapment are calculated (Fig. 4). The vol.% of the vapor phase within the vapor inclusions at 50 °C are also calculated and graphically represented (Fig. 4), in order to provide a visual estimation of what a vapor inclusion resulting from phase separation may look like at room temperature.

**Fig. 4.** Simulation of fluid phase separation from an H2O–CO2–NaCl parent fluid into a CO2-enriched vapor and a NaCl-enriched liquid, based on the equations of Duan et al. (1995). The volumetric proportions of the two phases and their compositions are shown for different T–P conditions. See text for more detailed explanation.

For an initial composition of H2O = 0.9, CO2 = 0.07, and NaCl = 0.03 (point a, Fig. 4), phase separation is not possible at temperatures >350 °C. At T = 300 °C and P = 1, 2, and 3 kbar, phase separation produces 22.3–31.3% vapor and 68.7–77.7% liquid, and the vapor phase contains 0.518–0.697 mole fraction of H2O, which produces a significant portion of aqueous phase at 50 °C (Fig. 4).

For a fluid of H2O = 0.8, CO2 = 0.16, and NaCl = 0.04 (point b, Fig. 4), phase separation is not possible at temperatures >400 °C. At T = 350 °C phase separation does not take place at P = 1 kbar, but does so at P = 2 and 3 kbar. Phase separation produces 21.1–22.1% vapor and 77.9–78.9% liquid. At T = 300 °C, phase separation...
takes place at \( P = 1, 2, \) and 3 kbar, producing 42.2–48.1% vapor and 51.9–57.8% liquid. At both temperatures, the vapor phase contains significant amounts of water (0.345–0.472 mole fraction), yielding an obvious aqueous rim in the vapor inclusions at 50 °C (Fig. 4).

With increasing CO\(_2\) contents in the initial fluid to a composition of H\(_2\)O = 0.48, CO\(_2\) = 0.48, and NaCl = 0.04 (point c, Fig. 4), phase separation can take place from \( T = 300 \) to 500 °C and \( P = 1–3 \) kbar. The vapor phase resulting from phase separation takes 57.3–91.9 volume\%, and has H\(_2\)O contents from 0.221 to 0.467 mol fractions. A rim of aqueous phase in the vapor inclusions can be visible at 50 °C (Fig. 4).

With further increase of CO\(_2\) contents to H\(_2\)O = 0.16, CO\(_2\) = 0.80, and NaCl = 0.04 (point d, Fig. 4), phase separation can take place from \( T = 300 \) to 400 °C and \( P = 1–3 \) kbar. At \( T = 500 \) °C, phase separation cannot take place for \( P = 1 \) kbar, but can for \( P = 2 \) and 3 kbar. The vapor phase resulting from phase separation is volumetrically dominant (94.1–96.9%), and the liquid phase is minor (3.1–5.9%). Water contents in the vapor phase range from 0.000 to 0.148 mol fraction, and an aqueous phase rim may be absent or minor in the vapor inclusions at 50 °C (Fig. 4).

The modeling results indicate that although phase separation is generally possible for the H\(_2\)O–CO\(_2\)–NaCl system and can produce a relatively CO\(_2\)-enriched vapor phase, there are important restrictions on the composition of the initial fluid and pressure–temperature conditions in order to produce a H\(_2\)O-poor, CO\(_2\)-dominated vapor phase. An initially H\(_2\)O-rich fluid (cases a and b, Fig. 4) can only experience phase separation at temperatures below 400 °C, and the vapor phase thus produced contains significant amounts of H\(_2\)O. An initial fluid with equal amounts of H\(_2\)O and CO\(_2\) (case c, Fig. 4) can experience phase separation at the pressure–temperature conditions interpreted for the Campbell-Red Lake deposit, but cannot produce a vapor that is poor in water. It appears that an initially CO\(_2\)-dominated fluid, with \( X_{CO_2} > 0.8 \), is required to produce a H\(_2\)O-poor, CO\(_2\)-dominated vapor. Two mechanisms have been previously proposed by Crawford and Hollister (1986) to explain the entrapment of CO\(_2\)-dominated fluid inclusions without co-existing aqueous inclusions. Firstly, the CO\(_2\)-dominated phase can be entrapped as “impurities” as crystals grow (primary inclusions), whereas the aqueous phase that wets the crystal phase may remain outside the advancing crystal front without being entrapped. Secondly, capillary action may “wick” the aqueous phase out of microfractures (due to its low wetting angles), leaving behind the CO\(_2\)-dominated phase entrapped as CO\(_2\)-dominated inclusions (pseudosecondary and secondary). However, these mechanisms alone cannot explain the rarity of aqueous inclusions, as indicated by the common occurrences of both aqueous and carbonic inclusions in most orogenic Au deposits. The CO\(_2\)-dominated nature of the initial fluid and consequently a small proportion (<5%) of aqueous phase being produced from phase separation, coupled with the above two mechanisms, may have been responsible for the rarity of aqueous inclusions in the mineralizing systems in the Red Lake greenstone belt.

5. \( CO_2 \) requirement and source constraints

Previous studies of the hydrothermal alterations related to Au mineralization in the Red Lake greenstone belt all indicate that CO\(_2\), S, Au, and K were added from the hydrothermal fluids to the host rocks (Andrews et al., 1986; Parker, 2000), which is similar, but not unique, to most orogenic Au deposits (Groves et al., 2003; Goldfarb et al., 2005; Dubé and Gosselin, 2007). It should be intriguing to calculate how much CO\(_2\) was input to the Red Lake greenstone belt in relation to Au mineralization, and how large a source area is required to produce the amount of CO\(_2\) that passed through the greenstone belt and resulted in the observed carbonaceous alteration. Because carbonate alteration (and veining) is not evenly distributed in the Red Lake greenstone belt, it is very difficult to make an estimate of the total amount of CO\(_2\) being added to the whole greenstone belt. However, it is possible to have an order-of-magnitude estimate for individual deposits. Since the Campbell-Red Lake deposit is the largest deposit in the region, contributing 840 t out of about 1000 t Au for the greenstone belt, the calculations are focused on this deposit.

Two methods can be used to estimate the amounts of CO\(_2\) being added to a deposit. One is based on estimate of the volume of the mineralized zone (including the non-economic alteration part) and the average CO\(_2\) content, as used by Phillips et al. (1987) for the giant Golden Mile Au deposit, Kalgoorlie, Australia. The other relies on estimation of the amount of fluids passing through the mineralization zone and the deposition efficiency of CO\(_2\), with the amount of fluid being calculated based on the amount of metal deposited and assumptions of metal solubility and deposition efficiency. The second method has large uncertainties associated with it, but it can provide important constraints on Au solubility and the source regions. The calculation results for the Campbell-Red Lake deposit and assumptions associated with them are listed in Table 3 and explained in detail below.

The mineralization + alteration zone of the Campbell-Red Lake deposit is about 2 km long, 250 m wide, and 2 km deep. Carbon dioxide contents range from 28.5 to 42.9 wt.% in ankerite veins (Parker, 2002), 6.5–20.9 in carbonate breccia (Cadièux et al., 2006), and 5.2–13.6 wt.% in the carbonate–biotite alteration envelope (Cadièux et al., 2006) or 7.3–23.6 wt.% in altered ultramafic rocks (Tarnocai, 2000). Other alteration rocks (alumino alteration and garnet–magnetite alteration), however, contain as little CO\(_2\) as <0.18–3.5 wt.% (Cadièux et al., 2006). Due to lack of systematic chemical analysis across the mineralization + alteration zone, the total amount of CO\(_2\) cannot be determined with certainty. However, based on the rather small number of analyses, it seems an average CO\(_2\) content of 10 wt.% is probably within the order-of-magnitude range. Using this tentative value and a rock density of 2.9 g/cm\(^3\) (as used by Phillips et al., 1987 for Golden Mile), the total amount of CO\(_2\) in the Campbell-Red Lake mineralization zone is 290 Mt (case a, Table 3). For comparison, Phillips et al., 1987 used a CO\(_2\) content of 11% for the chlorite zone and 14% for the carbonate zone in their calculation of total CO\(_2\) input in the Lake View mine, which led to an estimation of total CO\(_2\) amount of 340 Mt for the Golden Mile deposit.

The next four cases (cases b–e, Table 3) are based on the calculation of the amount of fluid flowing through to deposit 840 t Au in the Campbell-Red Lake deposit. Parameters used in the calculations are varied with reference to a Au solubility of 2 μg/L, a Au deposition efficiency of 80%, and a CO\(_2\) deposition efficiency of 10%. The low Au solubility value is chosen for reference based on an estimation by Seward and Barnes (1997) for vein-type Au deposits (1–10 μg/L) and on measurements of Au in some modern hydrothermal solutions (<0.1–23 μg/L; Simmons and Brown, 2008). The Au and CO\(_2\) deposition efficiency values are considered by Phillips et al. (1987) as “best estimate” for the Golden Mile deposit based on thermodynamic calculations by Neall (1985), which indicate no significant change in the activity of CO\(_2\) and a drop of Au concentration in the solution by more than 90% across alteration zones. \( X_{CO_2} \) is assumed to be 0.8 (i.e., 91 wt.% CO\(_2\)) based on observations of fluid inclusions and phase separation modeling discussed above.

Assuming a Au solubility value of 2 μg/L, the total amount of mineralizing fluid passing through the Campbell-Red Lake deposit is calculated as \( \text{Fluid} = \frac{840 \times 10^3}{0.002 \times 10^3} = 5.25 \times 10^{11} \) (t). This amount of fluid contains \( 5.25 \times 10^{11} \) t × 91% = 4.78 × 10^{11} (t) of CO\(_2\). Since the deposition efficiency of CO\(_2\) is 10%, the total amount of CO\(_2\) deposited is 4.78 × 10^{11} (t) × 10% = 4.78 × 10^{10} (t) = 47,800 Mt. This
amount (case b, Table 3) is two orders of magnitude higher than the estimation of case a, which is considered to be more plausible. To reduce this large discrepancy, significant changes must be made to case b: either the Au solubility is two orders of magnitude higher (i.e., 200 µg/L; case c, Table 3), or the CO2 deposition efficiency is two orders of magnitude lower (i.e., 0.1%; case d, Table 3), or a combination of the two (gold solubility = 20 µg/L, CO2 deposition efficiency = 1%; case e, Table 3). In each of these cases, the amount of CO2 deposited would be 478 Mt, which is within the same order-of-magnitude as case a.

The above different scenarios have very different implications on the source regions. Using again the “best estimate” of the source regions by Phillips et al., 1987: CO2 concentration in source rock = 1%; CO2 extraction efficiency = 60%; Au extraction efficiency = 80%; source rock density = 3 g/cm³.

Table 3
Estimations of the total amount of CO2 input in the Campbell-Red Lake Au deposit and source requirements.

<table>
<thead>
<tr>
<th>CO2 requirement</th>
<th>CO2 (Mt)</th>
<th>Assumptions</th>
<th>Source rock Au (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Total amount of CO2 based on estimated vein and altered rock volume and average CO2 content in the Campbell-Red Lake mineralization + alteration zone</td>
<td>290</td>
<td>The mineralization + alteration zone = 2000 m long, 250 m wide, and 2000 m deep; rock density = 2.9 g/cm³; average CO2 concentration = 10 wt.%</td>
<td>19.7</td>
</tr>
<tr>
<td>Total amount of CO2 based on total Au input (840 t) and assumptions about Au solubility and deposition efficiency, CO2 deposition efficiency, and XCO2 = 0.8 (~91 wt.%)</td>
<td>47,800</td>
<td>Au solubility = 2 µg/L; Au deposition efficiency = 80%, CO2 deposition efficiency = 1%</td>
<td>0.1</td>
</tr>
<tr>
<td>(b) Assuming very low Au solubility</td>
<td>478</td>
<td>Au solubility = 200 µg/L; Au deposition efficiency = 80%, CO2 deposition efficiency = 10%</td>
<td>11.9</td>
</tr>
<tr>
<td>(c) Assuming very high Au solubility</td>
<td>478</td>
<td>Au solubility = 2 µg/L; Au deposition efficiency = 80%, CO2 deposition efficiency = 0.1%</td>
<td>0.1</td>
</tr>
<tr>
<td>(d) Assuming very low CO2 deposition efficiency</td>
<td>478</td>
<td>Au solubility = 20 µg/L; Au deposition efficiency = 80%, CO2 deposition efficiency = 1%</td>
<td>1.2</td>
</tr>
<tr>
<td>(e) Moderately high Au solubility and low CO2 deposition efficiency</td>
<td>528</td>
<td>Total CO2 flowing through = 47,800 Mt; deposition efficiency = 1 wt.%</td>
<td></td>
</tr>
</tbody>
</table>
solubility significantly higher than usually assumed (a few μg/L), e.g., 200 μg/L, is required.

6. Discussion

The relationship between the CO₂-dominated mineralizing fluids and alterations (especially those involving hydrous minerals such as biotite, sericite, and chlorite) needs to be discussed. The CO₂-dominated nature of the fluids may be reflected by XCO₂ values calculated from alteration mineral assemblages, which are broadly contemporaneous with peak metamorphism. XCO₂ values from 0.45 to 0.85 have been obtained by Damer (1997) for the Red Lake mine. These values are significantly higher than those for most orogenic Au deposits (0.05–0.25; McCuaig and Kerrich, 1998), and are consistent with the unusually CO₂-dominated nature of fluids as indicated by fluid inclusions. However, the XCO₂ values calculated from mineral assemblages are not necessarily the same as the fluids passing through the main conduits (fractures now filled by veins). Tarnocai (2000) noticed an increase of XCO₂ from 0.025 in rocks distal to auriferous veins to 0.45 adjacent to the veins in the Campbell mine. It is likely that the CO₂-dominated fluids, which were probably advected from a deeper part of the crust, are mainly confined in fluid conduits, whereas H₂O-dominated fluids, which may have been derived from the ambient environment, become increasingly important away from the conduits (Fig. 5). Therefore, the CO₂-dominated nature of the mineralizing fluids is not inconsistent with the development of hydrous alterations in the host rocks. Such a profile of decreasing XCO₂ values away from the conduits may be present both in the proximal ferroan dolomite zones and in the distal calcite zones.

Helium isotopes of fluid inclusions from the Campbell-Red Lake deposit indicate that the fluids were derived from a crustal source (Chi et al., 2006). It is known that the CO₂ contents of metamorphic fluids generally increase with metamorphic grades (Crawford, 1981; Crawford and Hollister, 1986) and CO₂-dominated fluid inclusions are commonly found in granulite facies rocks and associated granitoids (Touret, 1981; Santosh et al., 2005). It is proposed here that the CO₂-dominated fluids in the Red Lake greenstone belt were derived from granulite facies source rocks, and were expelled upward along major structures, passing through the amphibole facies rocks, where the ambient fluids have moderate XCO₂, and then to the greenschist facies rocks with low XCO₂ (Fig. 5). A gradient of XCO₂ may be established across the conduits as the CO₂-dominated fluids passed through host rocks with lower XCO₂ values (Fig. 5).

The dominance of CO₂-dominated fluids within the conduits may have lasted longer in major hydrothermal-deformation corridors such as the Red Lake Mine trend hosting the Campbell-Red Lake and Cochenour deposits, and was relatively short-lived in less deformed zones such as the Redcon prospect and the Sandy Bay – Woodland Cemetery outcrop, where more aqueous fluid inclusions are found as secondary inclusions, indicating incursion of the ambient H₂O-dominated fluids.

Because the solubilities of carbonate minerals, unlike most other minerals, increase with decreasing temperature, the precipitation of carbonate minerals cannot have been caused by cooling of hydrothermal fluids (Kerrich and Fyfe, 1981). Two mechanisms may be envisaged to explain the deposition of large amounts of carbonate in the veins. The first one calls for the mixing of a H₂O-poor, CO₂-dominated fluid with an aqueous fluid containing Ca²⁺, Fe²⁺ and Mg²⁺, and the reactions involved are as follows:

\[ \text{CO}_2(g) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \quad (1) \]

\[ \text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \quad (2) \]

\[ \text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+ \quad (3) \]

\[ \text{Ca}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CaCO}_3 \quad (4) \]

Whether calcite or ankerite was precipitated depends on the contents of Ca²⁺, Fe²⁺ and Mg²⁺ in the aqueous solution, which may have been locally derived from the host rocks (Kerrich and Fyfe, 1981). Continuous input of CO₂, however, is unfavorable for carbonate precipitation because it will cause a pH decrease through reactions 1–3 above. In order for carbonates to continue

![Fig. 5. A sketch cross-section showing the distribution of different kinds of fluids in different crustal levels. CO₂-dominated fluids were derived from the granulite facies, and were channeled along major structures and then delivered to lower-order fractures. Fluids in the amphibole facies have moderately low XCO₂, whereas those in the greenschist facies are dominated by H₂O. Fluids of intermediate XCO₂ values resulted from mixing between CO₂-dominated fluids and ambient fluids of lower XCO₂ values. Note the XCO₂ profile shown in this figure may be present both in the proximal ferroan dolomite zones and the distal calcite zones.](image)
precipitation, H+ must be consumed by some water-rock interactions. Such reactions are recorded by potassic (sericite/muscovite or biotite) alteration accompanying carbonatization (Parker, 2000).

The second mechanism of carbonate precipitation is by phase separation of a fluid initially containing CO2, Ca2+, Fe2+ and Mg2+. The reaction involved may be expressed as

\[ \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2(\text{g}) \leftrightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- \quad (5) \]

A loss of CO2 through phase separation will cause the reaction to proceed toward the left and precipitation of calcite. It is possible that both fluid mixing and phase separation were involved in the precipitation of carbonates in the veins.

Although Au mineralization is spatially associated with carbonate veining (the proximal ferroan dolomite zone of Parker, 2000), it has been shown that Au deposition is closely associated with silica and sulfides (especially arsenopyrite) which, at least in part, replace carbonates. However, this does not mean that all Au mineralization postdates carbonate veining, because some carbonate ± quartz veins cut Au mineralized zones (Dubé et al., 2002). The spatial association between carbonate and Au mineralization has been related to the increased competency of the country rocks due to carbonatization that enhances brittle fracture and Au veining (Goldfarb et al., 2005). It may also be due to the common structural control of the fluid causing carbonate veining and that responsible for Au deposition, even if the two fluids are not genetically related. However, based on similarity of fluid inclusions in ankerite and Au-associated quartz, it is likely that the fluids that deposited Au, silica and sulfides are part of the same evolving (or protracted) hydrothermal system responsible for precipitating the carbonate ± quartz veins. The reason that the bulk of the carbonate deposition predates silification and Au deposition is probably that carbonate becomes oversaturated at higher temperatures than Au and silica. As temperature continues to decrease following carbonate deposition, Au and silica became oversaturated and were deposited, whereas carbonates were locally dissolved due to their increased solubility caused by decreased temperature. This may explain the partial replacement of carbonate ± quartz veins by silica, sulfides and Au.

The association of CO2-dominated fluid inclusions and Au mineralization in the Red Lake greenstone belt implies that Au can be transported by H2O-poor, CO2-dominated fluids. Carbon dioxide by itself is not an important agent for Au transport because it is a non-polar molecule. Trace amounts of H2S were detected by laser-Raman on individual inclusions (<0.1 mol%) and by gas chromatography on bulk inclusions (not quantified) in the Campbell-Red Lake deposit (Chi et al., 2006), and it has been postulated that Au may have been transported as AuHS- complexing or as H2S-solubilized species having the stoichiometry Au.n(H2S)mol (Chi et al., 2005, 2006). Zeein et al. (2007) have shown that gold can be dissolved in H2S gas as AuS(H2S)n or AuH(S)2H(S)n. Loucks and Mavrogenes (1999) demonstrated experimentally that at high temperature (550–725 °C) and pressure (1–4 kbar) conditions, Au is transported as AuH(S)2H(S)n, and therefore dissolved H2S gas that is ineffective in metal complexing at low pressures is highly effective at high pressures. Gold solubility at these high pressure-high temperature conditions can be extremely high, up to several hundreds of mg/L (Loucks and Mavrogenes, 1999).

The capacity of CO2-rich fluids to transport metals has also been demonstrated by the presence of chalcopyrite daughter mineral in CO2-rich fluid inclusions (Lai and Chi, 2007). The calculations on CO2 requirement and source constraints for the Campbell-Red Lake deposit, as shown above, suggest that Au solubility was likely in the order of several hundreds of μg/L, which appears unusually high compared to the common assumption of only a few μg/L of Au in ore-forming fluids (Seward and Barnes, 1997) but is possible in light of Loucks and Mavrogenes (1999) experiments. The high Au solubility may also explain why the Campbell-Red Lake deposit has such a high-grade of Au (average 21 g/t for the whole deposit, and average 80.6 g/t for the Goldcorp High-Grade zone).

The well developed colloform–crustiform structures in the carbonate ± quartz veins have been interpreted as indicating epithermal mineralization environments (Penczak and Mason, 1997, 1999) or a relatively shallow (epizonal) crustal level (possibly 2–5 km from surface) similar to the high-level orogenic systems at Wiluna, Australia (Dubé et al., 2002, 2004). However, crossingcutting relationships and isotopic dating suggest that the main phase Au mineralization, and at least part of the carbonate veining, occurred broadly during regional metamorphism, which took place at pressures from 2 to 4 kbar, corresponding to depths of 7–14 km (Thompson, 2003). Carbonic fluid inclusions with very low homogenization temperatures (as low as −12.6 °C, Table 1) in ankerite are consistent with the interpreted large pressures and depths. It is speculated here that the apparent conflict between colloform–crustiform structures and deep formation environments indicated by fluid inclusions may be related to the unusual high CO2 contents in the hydrothermal fluids. It is known that CO2-dominated fluids have high wetting angles (Watson and Brenan, 1987), which prevent interconnection of fluid phase in the host rocks and thus enhance the brittle properties of the rocks. The development of colloform–crustiform structures may also be related to extremely high fluid pressures which helped create high dilution rates favorable for forming open-space filling structures (Dubé et al., 2002).

7. Conclusions

In conclusion, fluid inclusion studies indicate that CO2-dominated fluids were involved in carbonate ± quartz vein formation and Au mineralization not only in the Campbell-Red Lake Au deposit, but also in small Au occurrences and non-mineralized veins in the Red Lake greenstone belt. Fluid phase separation modeling indicates that the CO2-dominated fluids likely have XCO2 values > 0.8. Hydrothermal mineral assemblages in the host rocks indicate XCO2 values as high as 0.45–0.85, indirectly supporting the CO2-dominated nature of the hydrothermal fluids. However, XCO2 values in the host rocks are generally lower than in the veins and have the tendency to decrease away from the veins. This indicates that the CO2-dominated fluids are mainly confined in fractures (veins), which may have migrated laterally into the host rocks and mix with H2O-dominated fluids, resulting in intermediate XCO2 values. The CO2-dominated fluids may have been derived from granulite facies in deeper parts of the crust, whereas H2O-dominated fluids were dominant in the ambient host rocks of amphibole and greenschist facies. Carbonate deposition may be related to fluid phase separation or mixing between CO2-dominated fluids and H2O-dominated fluids carrying Ca2+, Mg2+ and Fe2+. The fluids depositing carbonates were probably part of the same evolving and protracted large scale hydrothermal system precipitating SiO2 and Au: the bulk of the carbonates precipitated first at relatively high temperatures, became partly dissolved at lower temperatures (due to increased solubility), when SiO2 and Au were deposited and partly replaced carbonates. Mass balance calculations indicate that in order to deposit the speculative amount of CO2 (290 Mt) and the total amount of Au (840 t) in the Campbell-Red Lake deposit from the same evolving large scale hydrothermal fluid, the Au solubility in the fluid must be around 200 μg/L, which is two orders of magnitude higher than the usually assumed values of a few μg/L. The high Au contents of the CO2-dominated fluids may have been responsible for the high-grades of Au in the Campbell-Red Lake deposit.
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References


