SCHWEIZ. MINERAL. PETROGR. MITT. 72, 129–134, 1992

Fluid inclusion studies of the high-grade Ashuanipi Complex, Superior Province, Canada: retrograde P-T path and conditions of gold formation*, **

by *Robert Moritz*[1] and *Serge Chevé*[2]

Abstract

Gold-bearing Algoma-type iron formations and their high-grade metamorphic host rocks of the Ashuanipi Complex, Superior Province, Canada, have been the subject of a microthermometric fluid inclusion study. Isochores calculated for early CO_2-rich fluid inclusions, in conjunction with published geothermobarometric data, indicate a clockwise retrograde P-T-t path for the Ashuanipi Complex. Late low salinity H_2O fluid inclusions are spatially associated with gold showings and yield isochores which suggest, together with arsenopyrite thermometry and metamorphic petrology, that gold was precipitated, at least partially, during post-peak metarmorphic cooling and uplift. One of the gold occurrences is characterized by CH_4–N_2-rich fluids which could be responsible for the main gold deposition event or for secondary gold enrichment processes in that showing.

Keywords: Fluid inclusions, gold mineralization, metamorphism, Ashuanipi Complex, Superior Province, Canada.

Introduction

The Ashuanipi Complex is a high-grade metamorphic terrane of the eastern Superior Province in the Canadian Shield (CARD, 1991), and it is host to several sub-economic gold occurrences (CHEVÉ et al., 1989). The aim of the present microthermometric fluid inclusion investigation is twofold. First, this study seeks to constrain the retrograde pressure-temperature (P-T) path of the Ashuanipi Complex and compare this path to other high-grade metamorphic subprovinces of the Superior Province, such as the Kapuskasing structural zone. Second, in conjunction with other P-T indicators, this study aims at defining the P-T conditions and the relative timing of gold mineralization within the tectonic evolution of the Ashuanipi Complex.

Geologic setting

The geology of the Ashuanipi Complex is dominated by metatexite with interlayered homogenous and heterogeneous diatexite. Several stages of igneous activity have affected the Ashuanipi Complex, including tonalitic to granodioritic intrusions, nepheline syenites, and late mafic dikes. U–Pb ages indicate that the metasedimentary rocks and minor metavolcanic rocks were deposited prior to 2700 Ma. The main event of high-grade metamorphism (upper amphibolite and granulite facies), accompanied by intense migmatization, took place between 2650 and 2670 Ma. Cooling from the metamorphic peak and retrogression are interpreted to have taken place from 2650 to 2639 Ma (MORTENSEN and PERCIVAL, 1987; CHEVÉ and BROUILETTE, 1991; PERCIVAL et al.,

* Contribution n°: 91-5110-22, Ministère de l'Energie et des Ressources du Québec, Canada.
** Extended abstract of a contribution presented at the annual meeting of the Swiss Society of Mineralogy and Petrology, Chur, October 10 and 11, 1991.
[1] Département de Minéralogie, Université de Genève, 13, rue des Maraîchers, CH-1211 Genève 4, Switzerland.
[2] INRS-Géoressources, 2700, rue Einstein, Sainte-Foy, Québec, G1V 4C7 Canada.

Tab. 1 Summary of microthermometric fluid inclusion data.

Regional scale:

Type 1: CO_2-rich fluid inclusions
- Tm CO_2: -64.5 – -56.6 °C (n = 109)
- Th CO_2: -48.0 – +29.1 °C (n = 108)

Type 2: low-temperature/high-salinity aqueous fluid inclusions (H_2O–NaCl–$CaCl_2$)
- Tm Ice: -35.1 – -12.0 °C (n = 23)
- Tm hydrohalite: -24.3 – -23.6 °C (n = 3)
- Th: +114 – +207 °C (n = 42)
- Tm halite: +140 – +160 °C (n = 8)

Gold occurrences, local scale:

Type 3: Subtype 3a: CH_4-rich fluid inclusions (Lac Lilois gold occurrence)
- Tm CH_4: -181.4 – -158.0 °C (n = 9)
- Th CH_4: -105.0 – -82.1 °C (n = 8)

Subtype 3b: CH_4–N_2-rich fluid inclusions (Arsène gold occurrence)
- Th (liquid): -116.0 – -110.5 °C (n = 9)
- Th (vapour): -114.4 – -98.3 °C (n = 8)
- $T_{sublimation}$: -64.4 – -59.6 °C (n = 5)

Type 4: high-temperature/low-salinity aqueous fluid inclusions (H_2O–NaCl)
- Tm Ice: -12.2 – -4.4 °C (n = 20)
- Th: +229 – +374 °C (n = 20)

Homogenization is to the liquid phase unless stated otherwise. Fluid inclusions were studied in quartz.

1991). Peak metamorphic conditions were constrained to 700–850 °C and 3.5–6.5 kbar based on geothermobarometry of garnet-orthopyroxene-plagioclase-quartz assemblages (PERCIVAL and GIRARD, 1988; PERCIVAL et al., 1991).

Local, metamorphosed Algoma-type iron formations, interbedded with metatexite, host small, sub-economic gold occurrences (CHEVÉ et al., 1989). The iron formations consist of alternating quartz bands and layers of magnetite or pyrigarnite, that include clinopyroxene-orthopyroxene-garnet-quartz-fine grained and disseminated pyrrhotite ± biotite ± graphite. Local retrograde metamorphism affects the iron formations, with the appearance of amphibole, calcite, quartz, chlorite, epidote, sericite, pyrite, and magnetite replacing pyrrhotite. The gold-bearing mineralization is typically characterized by pyrrhotite, arsenopyrite and pyrite accompanied by subsidiary löllingite, chalcopyrite and pentlandite, and in some rare occurrences by native gold. The highest gold grades tend to be associated with high arsenopyrite contents.

Fluid inclusion types and microthermometry

The fluid inclusion microthermometric data are summarized in table 1. Four types of fluid inclusions were recognized based on phase relationships at room temperature and heating and freezing behaviour. All types of inclusions occur along trails or in clusters, therefore all types are considered to be secondary inclusions. Type 1 inclusions are CO_2-rich fluids. With the exception of four inclusions, melting temperatures of CO_2 range between –58.8 °C and –56.6 °C which indicates a low content of other dissolved gases such as CH_4 or N_2. Type 2 inclusions are low-temperature/high-salinity H_2O fluids. Some of them are two phases (liquid and gas) at room temperature and some contain a third phase (halite crystal). Ice starts to melt at temperatures below –40 °C which indicates that additional cations besides Na^+ are in solution, such as Ca^{++} and Mg^{++}. Type 3 inclusions are CH_4–N_2-rich fluids. Two subtypes can be distinguished. The first subtype has melting and homogenization temperatures between –181.0 °C and –181.5 °C, and between –82.1 °C and –105.0 °C, respectively. Such melting behaviour is characteristic for CH_4-rich fluids. The second subtype shows homogenization to the liquid or vapour phase between –98.3 °C and –116.0 °C, and some inclusions show sublimation between –59.6 °C and –64.4 °C. Such microthermometric behaviour is diagnostic for CH_4- and/or N_2-rich fluids (VAN DEN KERKHOF, 1990). Type 4 inclusions are high-temperature/low-salinity H_2O fluids. Melting of ice starts around –21 °C which suggests that Na^+ is the dominant cation in solution. Melting temperatures of ice indicates salinities between 7 and 16 weight % NaCl equivalent.

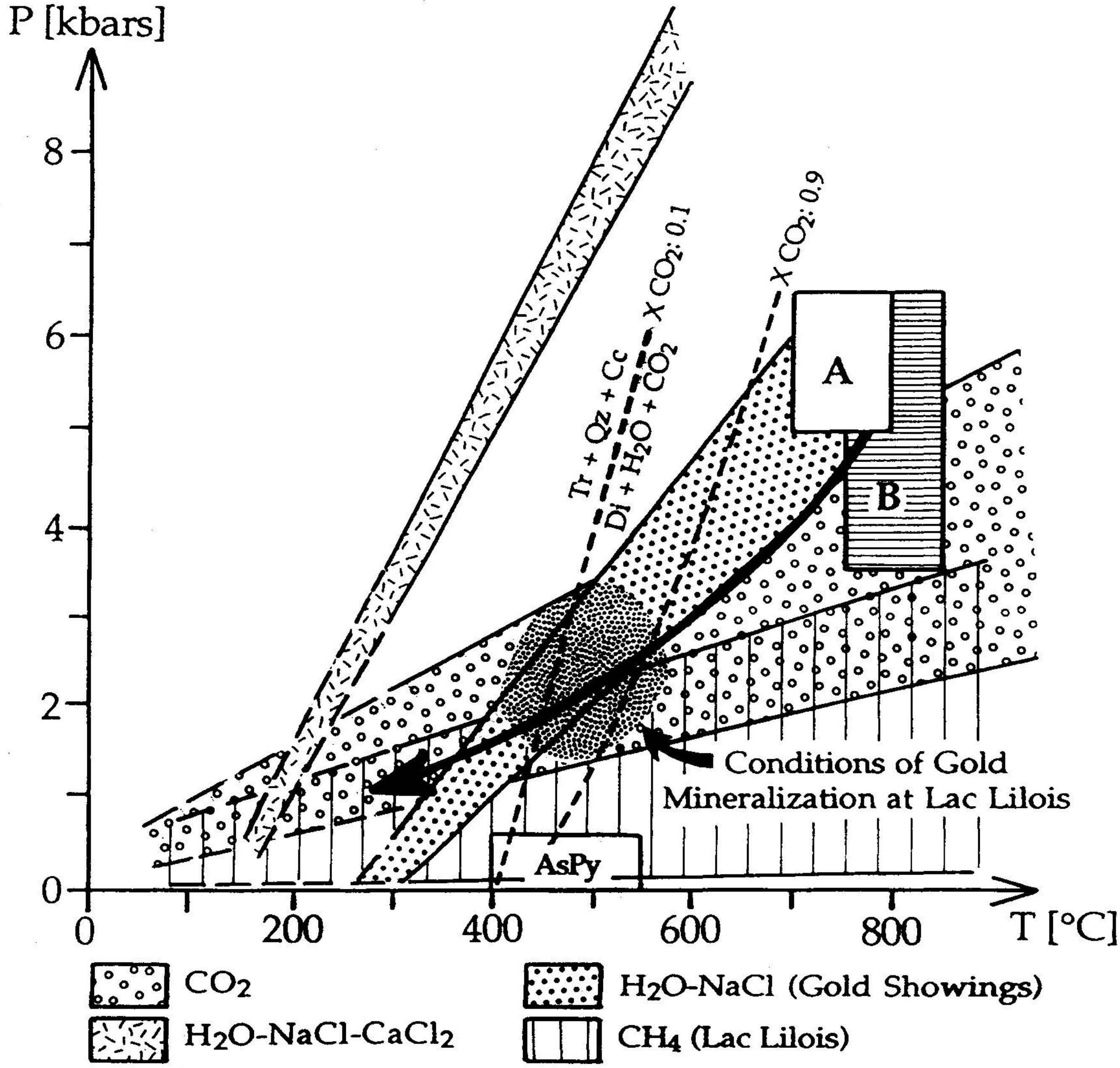

Fig. 1 Uplift and cooling path of the Ashuanipi Complex and conditions of gold mineralization inferred at the Lac Lilois occurrence. Isochores are plotted for the different fluid inclusion types described in the present study. Conditions of gold mineralization at the Lac Lilois occurrence are shown by the highly densed dotted area. The inferred uplift and cooling path is shown by the long arrow. The diopside (Di) + H_2O + CO_2 = tremolite (Tr) + quartz (Qz) + calcite (Cc) reaction lines are from SLAUGHTER et al. (1975) and have been traced for fluids with different CO_2-contents, i.e. XCO_2: 0.1 and XCO_2: 0.9. A and B are peak metamorphic conditions according to PERCIVAL and GIRARD (1988) and PERCIVAL et al. (1991), respectively. AsPy: preliminary temperature range based on arsenopyrite thermometry.

Distribution and origin of the fluids

Type 1 (CO_2-rich) fluids and type 2 (low-temperature/high-salinity H_2O) fluids occur regionally, whereas type 3 (CH_4–N_2-rich) fluids and type 4 (high-temperature/low-salinity H_2O) fluids have only been observed in gold occurrences. Type 1 (CO_2-rich) inclusions are the earliest trapped fluids. Such CO_2-rich fluids are characteristic of granulite facies terrains (TOURET, 1981). Since migmatization is widespread in the Ashuanipi Complex, a likely origin of the CO_2-rich fluids is by melting of the high-grade metamorphic rocks whereby the more soluble H_2O is dissolved in the

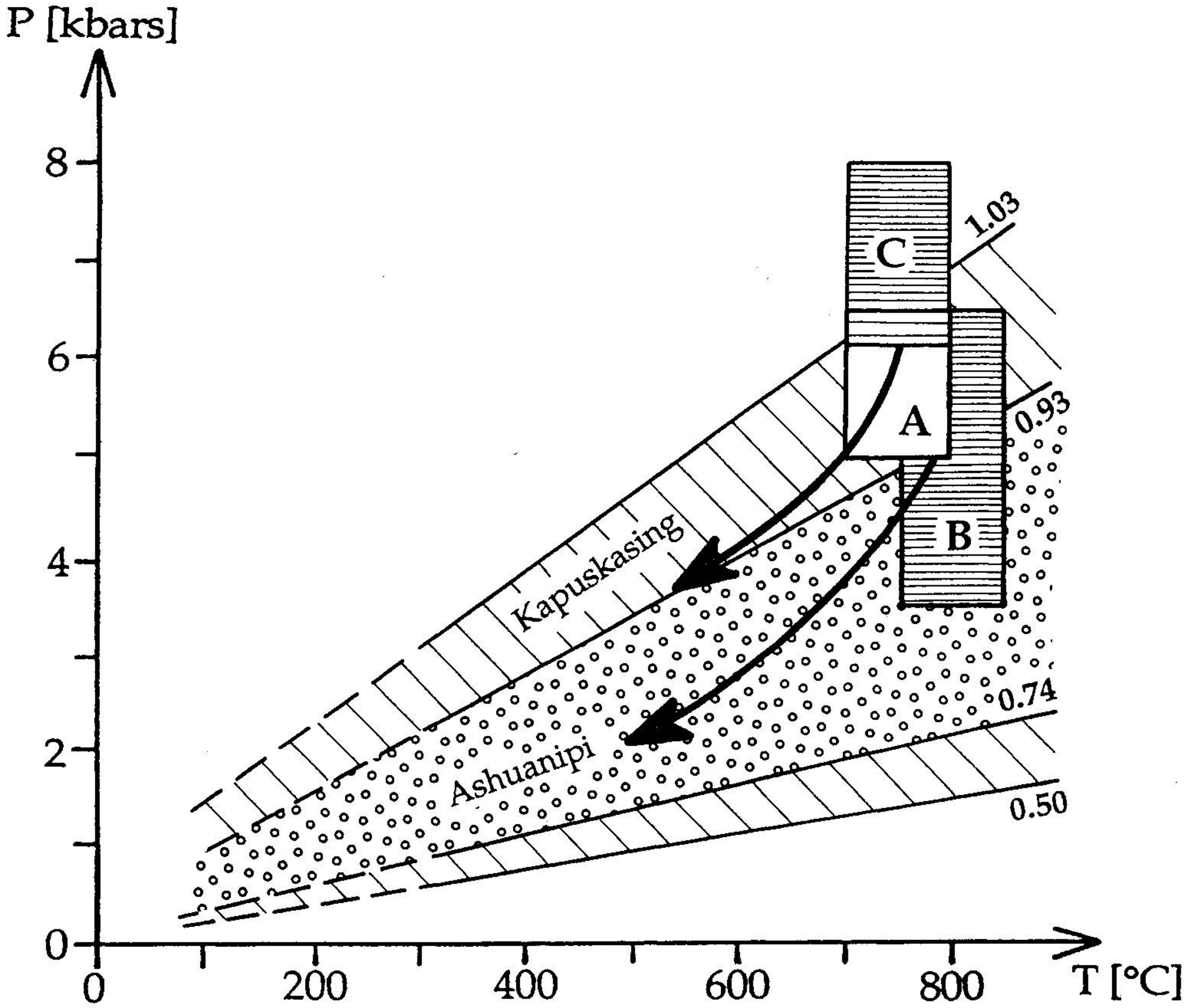

Fig. 2 Comparison of uplift and cooling paths of the Ashuanipi Complex and the Kapuskasing structural zone. Arrows show the uplift and cooling paths inferred from microthermometry on CO_2-rich fluid inclusions in the Kapuskasing structural zone (RUDNICK et al., 1984) and in the Ashuanipi Complex (present study). Isochores are in g/cm^3. A and B are peak metamorphic conditions in the Ashuanipi Complex according to PERCIVAL and GIRARD (1988) and PERCIVAL et al. (1991), respectively; and C are peak metamorphic conditions in the Kapuskasing structural zone according to PERCIVAL (1983).

molten fraction and then removed to shallower crustal levels, leaving CO_2 as a residual component (TOURET, 1981). Additionally, some of the CO_2 may originate from metacarbonates, the mantle, CO_2-bearing magmas or the oxidation of graphite. Type 2 (low-temperature/high-salinity H_2O) inclusions are similar to saline inclusions found elsewhere in the Canadian Shield (GUHA and KANWAR, 1987; HAYNES, 1988) and are generally interpreted as trapped brines of Proterozoic or Palaeozoic age (FRAPE et al., 1984). However, it is possible that some type 2 inclusions are trapped fluids generated during retrograde metamorphism. Type 3 ($CH_2 \pm N_2$-rich) inclusions may represent a fluid that has equilibrated with local graphite-rich rocks, such as pyrigarnite. Some of the CH_4 may also be the vapor component of an H_2O–NaCl–CH_4 fluid that has undergone phase separation, and some of the N_2 may be the product of mantle outgassing or breakdown of K-bearing minerals in which NH_4^+ substitutes for K. Finally, type 4 (high-temperature/low-salinity H_2O) inclusions may reflect decreasing P-T conditions in the Ashuanipi Complex from granulite to amphibolite-greenschist facies conditions, where H_2O predominates over CO_2 (TOURET, 1981).

Retrograde P-T path

Type 1 (CO_2-rich) fluid inclusions yield isochores that pass through and below peak metamorphic conditions in the Ashuanipi Complex determined by PERCIVAL and GIRARD (1988) and PERCIVAL et al. (1991) (Fig. 1). This suggests that these inclusions record syn- to post-peak metamorphic P-T conditions and indicates a clockwise retrograde P-T-time path, as is common in most granulite terranes (TOURET, 1981). According to PERCIVAL (1989), granulites from the Superior Province can be separated into those having low- to moderate-pressure metamorphic assemblages (3.5–6.5 kbar) (e.g. Ashuanipi Complex) and those having high pressure assemblages (7.5–9 kbar) (e.g. Kapuskasing structural zone). In figure 2 we compare the microthermometric data obtained on CO_2-rich fluids from the Kapuskasing high-pressure granulites by RUDNICK et al. (1984) and from the Ashuanipi Complex (this study). The CO_2-rich fluids in both terranes yield isochores passing through and below peak metamorphic P-T conditions with similar clockwise P-T-time paths. Figure 2 also shows that our fluid inclusion investigation and that of RUDNICK et al. (1984) support the conclusion of PERCIVAL (1989) that the Kapuskasing zone represents a high-pressure granulite terrane and the Ashuanipi Complex is a low-pressure granulite terrane, in all probability reflecting two distinctive tectonic environments of granulite formation.

Implications for gold metallogeny

In the Ashuanipi Complex, the best gold grades tend to be associated with high arsenopyrite abundances. In addition, at one of the richest gold occurrences (Lac Lilois), some of highest grade zones are characterized by small quartz segregations or quartz veinlets. The clinopyroxene in proximity to such segregations/veinlets is partially replaced by amphibole, calcite and quartz. As mentioned above, type 4 (high-temperature/low salinity H_2O) inclusions are restricted to gold occurrences and yield isochores that pass through metamorphic reaction lines that apply to mineralogical transformations observed at the Lac Lilois occurrence, in a temperature range compatible with preliminary arsenopyrite thermometry at the same occurrence (Fig. 1). This led MORITZ and CHEVÉ (1991) to suggest that part of the gold in the Ashuanipi Complex was deposited in a P-T range of 1.5–3 kbar and 400–550 °C, that is at the greenschist-lower amphibolite facies transition.

Another gold occurrence (Arsène) is characterized by $CH_4 \pm N_2$-rich fluids. The association of gold occurrences with such fluids has been reported elsewhere (e.g. GUHA and KANWAR, 1987; BOTTRELL and MILLER, 1990; DE ALVARENGA et al., 1990). According to GUHA and KANWAR (1987) such CH_4-rich fluids could be responsible for late, secondary gold enrichment, whereas BOTTRELL and MILLER (1990) propose that leaching of NH_4^+ from local wall rocks and subsequent reaction with graphite could provide a reducing mechanism whereby gold would be deposited.

Conclusions

Four distinctive fluids have been recognized in the high-grade metamorphic rocks of the Ashuanipi Complex: (1) CO_2-rich fluids, (2) low-temperature/high-salinity aqueous fluids, (3) CH_4–N_2-rich fluids, and (4) high-temperature/low-salinity aqueous fluids. The two former are distributed regionally, whereas the two latter are restricted to local gold-bearing iron formations. The CO_2-rich fluids are the earliest trapped fluids, and they indicate a clockwise retrograde P-T-time path. In combination with the fluid inclusion of RUDNICK et al. (1984) in the Kapuskasing structural zone, the present study supports the suggestion by PERCIVAL (1989) that the Kapuskasing uplift contains high-pressure granulites whereas the Ashuanipi Complex contains low-pressure granulites. One of the gold occurrences, i.e. Arsène, was affected by late CH_4–N_2-rich fluids, that could have been involved in the main mineralization event, or that could have caused secondary gold enrichment. Fluid inclusion microthermometry, arsenopyrite thermometry and metamorphic petrology in another major gold occurrence, i.e. Lac Lilois, suggest that gold deposition took place, at least partially, during post-peak metamorphic cooling and uplift in a P-T range compatible with the amphibolite-greenschist transition, a setting similar to that of major mesothermal gold deposits (KERRICH and WYMAN, 1990).

References

ALVARENGA, C.J.S. DE, CATHELINEAU, M. and DUBESSY, J. (1990): Chronology and orientation of N_2–CH_4, CO_2–H_2O, and H_2O-rich fluid-inclusion trails in intrametamorphic quartz veins from the Cuiaba gold district, Brazil. Mineralogical Magazine 54, 245–255.

BOTTRELL, S.H. and MILLER, M.F. (1990): The geochemical behaviour of nitrogen compounds during the formation of black shale hosted quartz-vein gold deposits, north Wales. Applied Geochemistry 5, 289–296.

CARD, K.D. (1990): A review of the Superior Province of the Canadian Shield, a product of Archean accretion. Precambrian Research 48, 99–156.

CHEVÉ, S.R. and BROUILLETTE, P. (1991): Radiogenic age constraints on the geological evolution of the northeastern Ashuanipi Complex, New Quebec.

Geological/Mineralogical Association of Canada annual meeting, Toronto May 1991, Program with abstracts 16, A23.

CHEVÉ, S.R., BROUILLETTE, P. and MORITZ, R.P. (1989): Minéralisations aurifères dans le Complexe d'Ashuanipi au NW de Schefferville, Nouveau-Québec. Geological/Mineralogical Association of Canada annual meeting, Montréal May 1989, Program with abstracts 14, A119.

FRAPE, S.K., FRITZ, P. and MCNUTT, R.H. (1984): Water-rock interaction and chemistry of groundwaters from the Canadian Shield. Geochimica et Cosmochimica Acta 48, 1617–1627.

GUHA, J. and KANWAR, R. (1987): Vug brines-fluid inclusions: a key to the understanding of secondary gold enrichment processes and the evolution of deep brines in the Canadian Shield. In FRITZ, P. and FRAPE, S.K., eds, Saline Waters and Gases in Crystalline Rocks. Geological Association of Canada, Special paper 33, 95–101.

HAYNES, F.M. (1988): Fluid-inclusion evidence of basinal brines in Archean basement, Thunder Bay Pb–Zn–Ba district, Ontario, Canada. Canadian Journal of Earth Sciences 25, 1884–1894.

KERKHOF, A.M. VAN DEN (1990): Isochoric phase diagrams in the systems CO_2–CH_4 and CO_2–N_2: applications to fluid inclusions. Geochimica et Cosmochimica Acta 54, 621–629.

KERRICH, R. and WYMAN, D. (1990): Geodynamic setting of mesothermal gold deposits: an association with accretionary tectonic regimes. Geology 18, 882–885.

MORITZ, R.P. and CHEVÉ, S.R. (1991): P-T conditions and relative timing of gold mineralization at Lac Lilois, Ashuanipi Complex, eastern Superior Province, Canada. In PAGEL, M. and LEROY, J.L., eds, Source, Transport and Deposition of Metals, Proceedings of the 25th SGA anniversary meeting, Nancy 1991. A.A. Balkema, Rotterdam, Netherlands, 685–688.

MORTENSEN, J.K. and PERCIVAL, J.A. (1987): Reconnaissance U–Pb zircon and monazite geochronology of the Lac Clairambault area, Ashuanipi Complex, Quebec. Geological Survey of Canada, Paper 87-2, 135–142.

PERCIVAL, J.A. (1983): High-grade metamorphism in the Chapleau-Foleyet area, Ontario. American Mineralogist 68, 667–686.

PERCIVAL, J.A. (1989): Granulite terranes and the lower crust of the Superior Province. In MERAU, R.F., MUELLER, S. and FOUNTAIN, D.M., eds, Properties and Processes of Earth's Lower Crust. American Geophysical Union, Monograph 51, IUGG 6, 301–310.

PERCIVAL, J.A. and GIRARD, R. (1988): Structural character and history of the Ashuanipi Complex in the Schefferville area, Quebec-Labrador. Geological Survey of Canada, Paper 88-1C, 51–60.

PERCIVAL, J.A., MORTENSEN, J.K, STERN, R.A., CARD, K.D. and BÉGIN, N.J. (1991): The high-grade Ashuanipi and Minto subprovinces of the Superior Province. Geological/Mineralogical Association of Canada annual meeting, Toronto May 1991, Program with abstracts 16, A97.

RUDNICK, R.L., ASHWAL, L.D. and HENRY, D.J. (1984): Fluid inclusions in high-grade gneisses of the Kapuskasing structural zone, Ontario: metamorphic fluids and uplift/erosion path. Contributions to Mineralogy and Petrology 87, 399–406.

SLAUGHTER, J., KERRICK, D.M. and WALL, V.J. (1975): Experimental and thermodynamic study of equilibria in the system CaO–MgO–SiO_2–H_2O–CO_2. American Journal of Science 275, 143–162.

TOURET, J.L.R. (1981): Fluid inclusions in high grade metamorphic rocks. In HOLLISTER, L.S. and CRAWFORD, M.L., eds, Fluid Inclusions: Applications to Petrology. Mineralogical Association of Canada, Short course 6, 182–208.

Manuscipt accepted January, 9, 1992.