

# Carlin-type gold mineralization at Saint-André-de-Ristigouche, Gaspé Peninsula (Québec), Canadian Appalachians

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**Abstract** The Gaspé Peninsula, in the Canadian Appalachians, hosts a variety of mineral occurrences that are spatially associated with the Grand Pabos and Restigouche faults. Among these occurrences, the Saint-André-de-Ristigouche gold (SAR-Au) showing has peculiar features comparable with Carlin-type gold deposits at the regional, district, and prospect scales. The most striking ones are: (1) the calcareous nature of the host rocks; (2) the Au-As-Sb-Hg metallic signature with absence of base metals and Ag; (3) the association with a crustal scale fault zone; (4) the hydrothermal alteration characterized by silicification, calcite, and quartz veinlets at the margin of the Au-bearing zones and the occurrence of kaolinite in large halos of argillic alteration; (5) numerous felsic dikes; (6) the occurrence of Au in As-rich pyrite forming overgrowths on premineralization As-free pyrite, and in arsenopyrite; (7) hydrothermal fluids equilibrated with host rocks at high temperature (>200°), which cooled to precipitate arsenopyrite and then mixed with evolved meteoric water to precipitate stibnite in veins. Although the SAR-Au showing

is relatively small, analogies with Carlin-type mineralization encourage exploration in the Gaspé Peninsula and in similar settings elsewhere in the Appalachians.

**Keywords** SAR-Au showing · Carlin-type deposits · Canadian Appalachians

## Introduction

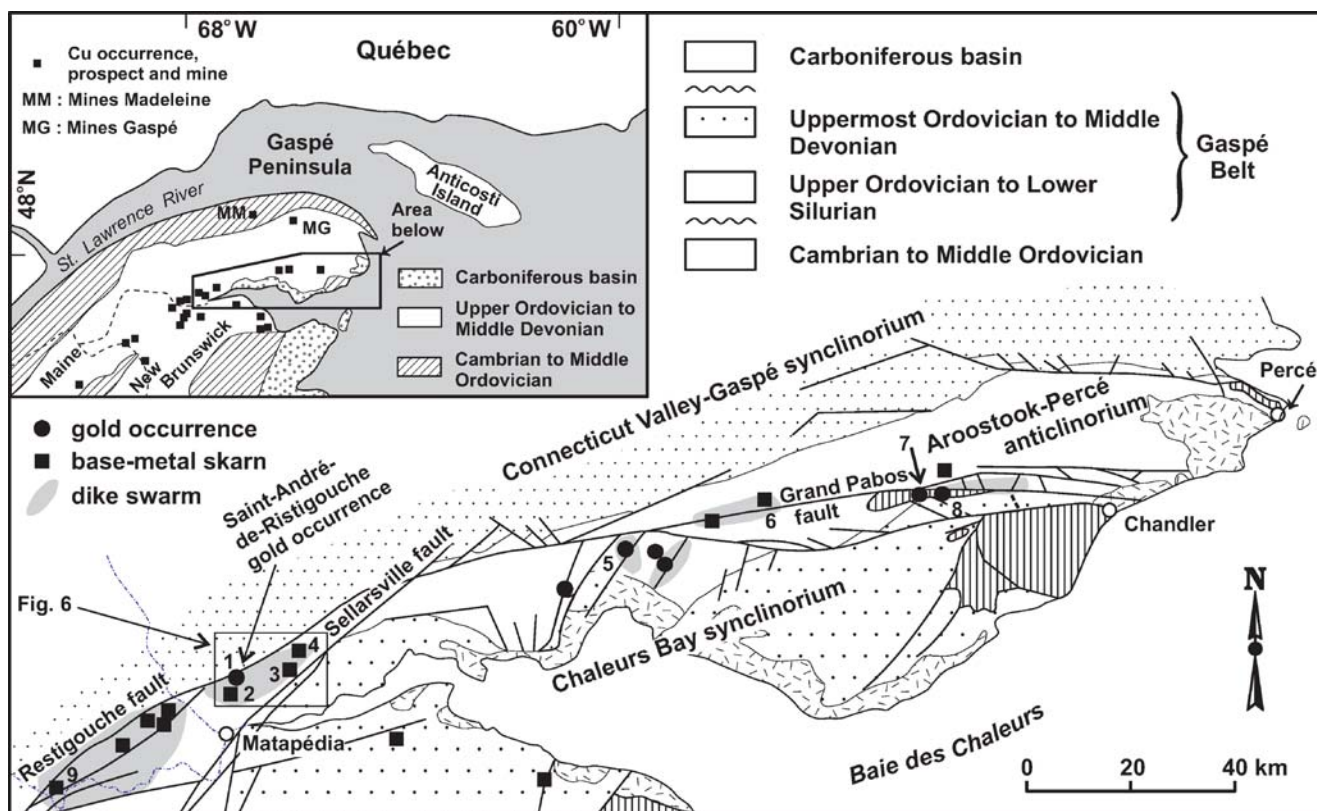
Major faults of the Canadian Appalachians host several types of gold mineralization (Gauthier et al. 1994; Swinden and Dunsworth 1995) including a variety of mineral occurrences that are spatially associated with the Grand Pabos and Restigouche faults in the Gaspé Peninsula (Fig. 1; Savard 1985; Malo et al. 1993). Polymetallic Cu-Pb-Zn-Ag-Au skarns and Au-bearing veins are the predominant styles of mineralization (Fig. 1). In addition, other mineral occurrences include serpentinite-hosted Ni-Cr occurrences, disseminated Zn-Pb-Cu-Ag and Ni occurrences in sandstone and mudstone, Cu occurrences in siltstone, and Pb-Zn occurrences in volcanic rocks (Savard 1985). Poulsen (1999a, b) suggested that geological environments, comparable to those hosting Carlin-type mineralization in Nevada, are present in southern Gaspé Peninsula (Québec) and in adjacent northwest New Brunswick. The metallogenic evolution of the Grand Pabos–Restigouche fault system was unravelled by detailed mapping (Malo et al. 1993), structural and paragenetic studies of skarns and Au-bearing veins (Chagnon 1984, 1988; Chagnon and Malo 1991; Malo et al. 1998), and lead isotopes data on galena (Moritz and Malo 1996). Malo et al. (1998, 2000) showed that the structural setting of the Saint-André-de-Ristigouche (SAR) gold showing, its metallic signature (Sb-Au-As±Hg), the nature of host rocks,

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**Fig. 1** Simplified geology of southern Gaspé Peninsula and location of the SAR-Au study area. Mineral occurrences: 1, SAR-Au showing; 2, Saint-André-de-Ristigouche Cu skarn; 3, Basket Brook Cu–Ag

skarn; 4, Saint-Fidèle Cu skarn; 5, Maria Au occurrence; 6, Reboul base-metal skarn and Au occurrence; 7, Lac Arsenault Au occurrence; 8, Weir Au occurrence. MG, Mines Gaspé; MM, Mines Madeleine

and the presence of argillic alteration in the southwestern Gaspé Peninsula were regional features similar to those of the Carlin-type deposits region in Nevada.

This paper presents the petrographic, mineralogical, and geochemical characteristics of the mineralized rocks and Au-bearing minerals of the SAR-Au showing. To compare SAR-Au showing with Carlin-type gold deposits from Nevada, it is necessary to determine the nature of Au-bearing minerals, as Carlin-type deposits are characterized by rims of As-rich pyrite containing disseminated gold, overgrown on (As, Au)-free pyrite cores in silicified limestones.

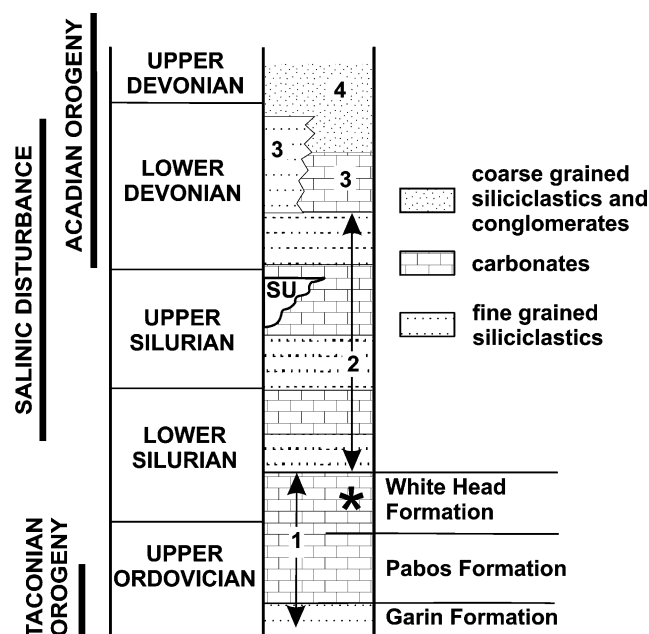
The SAR-Au showing consists in two subvertical stibnite-quartz-Au fault-filled veins, surrounded by a halo of silicification developed within the host limestones. Our detailed petrographic and geochemical study shows that SAR-Au showing presents several of the main characteristics of Carlin-type deposits, and more particularly (As–Au)-rich pyrite rims on (As, Au)-free pyrite cores, which is a distinctive characteristic of Carlin-type gold deposits. Fluid inclusion microthermometric analysis and stable isotope geochemistry highlight the temperature and compositional properties of the mineralizing fluids and their interpreted sources. The results show that the SAR shares strong similarities with Carlin-type gold deposits from

Nevada and represents the best example of this style of mineralization in the Gaspé Appalachians. In addition, new exploration targets are proposed, based on the structural, lithological and clay alteration features in the southwestern Gaspé Peninsula.

In this paper, the expression ‘Carlin-type’ gold deposits is preferred to ‘Carlin-like,’ as (1) ‘Carlin-like’ often refers to ‘distal-disseminated’ gold deposits (Berger and Bagby 1991; Tosdal 1999), (2) this study shows that the most important features characterizing Carlin-type gold deposits are found at SAR-Au showing, indicating that it is probably of Carlin affinity.

### Geological setting

The Gaspé Appalachians in the Gaspé Peninsula is made up of Paleozoic rocks, mainly sedimentary with minor volcanic rocks, which can be divided into three temporal rock assemblages (Figs. 1 and 2): (1) Early Cambrian (Latest Precambrian?) to Late Ordovician rocks; (2) Late Ordovician to Middle Devonian rocks, the Gaspé Belt, and (3) Carboniferous rocks. The first rock assemblage was deformed by both the Taconian (Late Ordovician) and the Acadian (Middle Devonian) orogenies, whereas the second



**\* location of Saint-André-de-Ristigouche gold occurrence**

**Fig. 2** Simplified stratigraphy of the study area adapted from Malo (2001). 1: Honorat and Matapédia Groups; 2: Chaleurs Group; 3: Upper Gaspé Limestones and Fortin groups; 4: Gaspé Sandstone Group; SU: Salinic unconformity

rock assemblage was deformed during the Acadian orogeny, but also recorded structural features linked to the Silurian Salinic disturbance (Malo and Kirkwood 1995; Malo et al. 1995; Malo 2001). Paleozoic rock assemblages remained largely unaffected by the Late Carboniferous–Permian Alleghanian orogeny.

### Gaspé Belt stratigraphy

The southern Gaspé Peninsula contains the Upper Ordovician–Devonian rocks of the Gaspé Belt (Malo and Bourque 1993), which is divided into three major structural zones, from north to south: (1) the Connecticut Valley–Gaspé synclinorium; (2) the Aroostook–Percé anticlinorium, and (3) the Chaleurs Bay synclinorium (Fig. 1; Bourque et al. 2001). In the Québec segment, the stratigraphy in the Gaspé Belt is composed of four broad lithostratigraphic units (Fig. 2): (1) Upper Ordovician–lowest Silurian deep-water, fine-grained siliciclastic and carbonate facies (Honorat and Matapédia groups); (2) Silurian–lowest Devonian shallow to deep shelf facies (Chaleurs Group); (3) Lower Devonian mixed, fine-grained siliciclastic and carbonate facies (Upper Gaspé Limestones and Fortin groups); (4) upper Lower to Middle Devonian near-shore to terrestrial coarse-grained terrigenous rocks (Gaspé Sandstones Group). Upper Silurian and Lower Devonian continental tholeiitic basalts and andesites occur in the upper part of the lithostratigraphic unit (2) and in lithostratigraphic units (3) and (4).

Rocks of the Gaspé Belt are bounded by two major angular unconformities. The oldest is between the Cambrian–Ordovician Taconian-deformed rocks and the base of the sequence, whereas the second is between the Acadian-deformed Gaspé Belt rocks and the overlying subhorizontal Carboniferous rocks. A Late Silurian unconformity, linked with Salinic synsedimentary block faulting, is recognized within the lithostratigraphic unit 2 (Fig. 2). The Gaspé Belt rocks were affected by regional anchi- to lower greenschist-grade (burial) regional metamorphism. Local zones of higher grade contact metamorphism are spatially associated with Devonian intrusions. Plutons are restricted to the northern part of the peninsula, whereas stocks and dike swarms are mainly emplaced along major Acadian faults (Doyon and Berger 1997), intrude the Gaspé Belt rocks further south (Fig. 1).

### Structural setting

The Grand Pabos fault with its western extension, the Restigouche fault, and their subsidiary faults form a major Acadian dextral strike-slip fault system of the Gaspé Belt (Fig. 1). The Grand Pabos fault consists of a 100-m wide high-strain zone with ductile deformation (Kirkwood and Malo 1993). The Acadian regional structural trend of the Gaspé Belt rocks is northeast. Major east- to east/northeast-trending dextral strike-slip faults cut this trend (Fig. 1). Regional Acadian folds are generally open and upright. Near major faults, folds are tight, steeply plunging and inclined to the northwest or the southeast. A regional northeast-trending cleavage is well developed throughout the Gaspé Belt. Northeast-trending faults are high-angle reverse faults, northwesterly directed in the northern Gaspé Belt and southwesterly directed in the south (e.g., the Sellarsville fault in southwestern Gaspé Peninsula; Fig. 1). Salinic structural features are related to the Late Silurian extensional tectonics before contractional Middle Devonian Acadian folding and faulting. These features are mainly synsedimentary normal faults and extensional longitudinal folds (Malo 2001). Alleghanian orogeny is expressed only by minor normal faults in southern Gaspé Peninsula (Fig. 1).

### Metallogeny

A number of gold prospects have been identified in the southern Gaspé Peninsula (Fig. 1). The most important are, from west to east: SAR, Maria, Reboul, Lac Arsenaault, and Weir (Fig. 1). Twelve base-metal skarn prospects and occurrences are also known in this area (Fig. 1; Savard 1985). Rocks of the Aroostook–Percé anticlinorium, more particularly limestones of the White Head Formation (lithostratigraphic unit 1 of the Gaspé Belt), host these base-metal skarns, as well as the SAR gold prospect. Three

of these base-metal skarns are found in the vicinity of the SAR (Saint-André-de-Ristigouche Cu skarn, Basket Brook Cu–Ag skarn, and Saint-Fidèle Cu skarn, Fig. 1).

At the regional scale, the Restigouche fault is straight, but local releasing bends are present as typically found in large-scale strike-slip faults (Sylvester 1988). The SAR-Au showing is located at a releasing bend highly visible on a very low frequency electromagnetic anomaly map (Daigle 1990). Gold mineralization is mainly found in stibnite-quartz-Au veins trending N130°, compatible with local extension related to the overall dextral displacement along the Restigouche fault. The mineralized veins fill extensional fractures and exhibit open-space filling textures (Malo et al. 1998). Gold is also present in As-rich pyrite overgrowths on As-free pyrite cores in strongly silicified calcilutite.

### Samples and analytical methods

The study area is about 18 km in length and 14 km wide in southwestern Gaspé Peninsula (Fig. 1). About 200 samples were collected from outcrops in creeks and along roads. In addition, more than 40 samples were collected in trenches at the SAR-Au showing from the main stibnite-quartz-Au vein and from altered limestones (Fig. 3). To better understand the geological context in which SAR-Au showing formed,

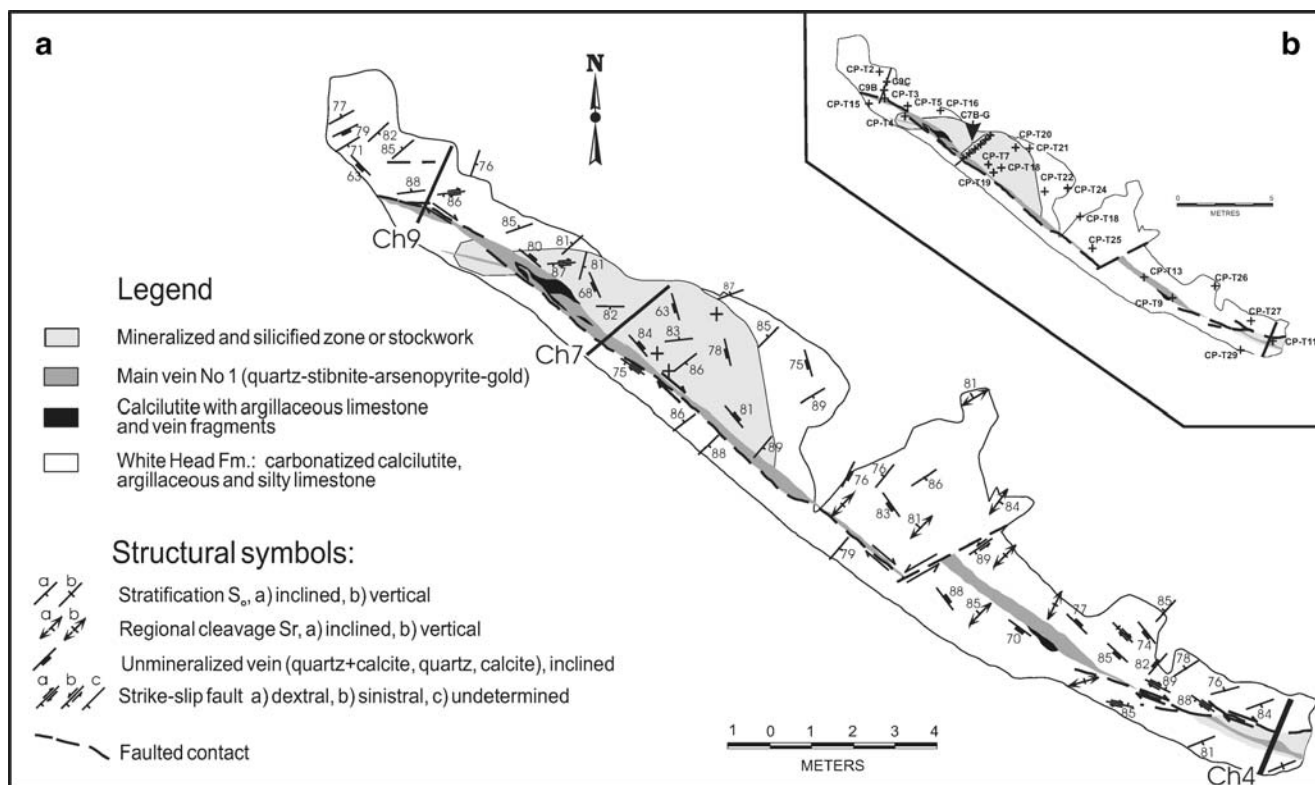
and to define prospecting guides, the alteration clay mineral assemblages were studied in a wider area including several Au and Cu prospects (Fig. 6).

### Whole-rock analyses

Whole-rock analyses were done by SGS Minerals (Ontario, Canada). Samples were crushed to 2 mm and powered in a chrome steel mill to <75 µm. Major elements contents were determined by X-ray fluorescence spectrometry. Au contents were analyzed by Lead Fire Assay with gravimetric finish when exceeding 2,000 ppb, on 30-g samples. Hg was analyzed by cold vapour, and Te by hydride atomic absorption spectrometry. Other trace-element contents were determined by Induced Coupled Plasma Mass Spectrometry.

### Clay mineralogy

The preparation of clay mineral concentrates was done at the INRS in Québec. Clay mineral concentrates were obtained by abrasion of rock fragments in demineralized water. The clay suspension was decarbonated in 1 N hydrochloric acid under constant agitation. The insoluble clay mineral residue was then separated by centrifuge into <2 µm and 2–16 µm granulometric fractions. X-ray diffraction analysis was performed on oriented mounts obtained by



**Fig. 3** Geology of the No.1 vein at SAR-Au showing. Modified from Pelchat (1995). Ch4 and Ch7 indicate the location of studied channel samples

sedimentation of clay suspensions onto glass slides, dried at room temperature, at Université Laval, Québec. Most samples were reanalyzed after saturation with glycerol. X-ray diffraction patterns were obtained on a Phillips diffractometer using  $\text{CuK}_\alpha$  radiation at 40 kV and 20 mA, a goniometer speed of  $2^\circ$   $2\theta/\text{min}$ , and digitalized and processed with the JADE software. The composition of illite and chlorite were evaluated by comparing the intensity ratios of their 002/001 and 004/003 reflections (Rey and Kübler 1983; Chagnon and Desjardins 1991).

#### Micro analytical techniques

Secondary electron and back-scattered electron images (BSE) were obtained with a JEOL-840-A Scanning Electron Microscope (SEM), and electron probe microanalyses (EPMA) were performed using the Cameca SX100 of Université Laval, Québec. Pyrite and arsenopyrite crystals were analyzed by EPMA under acceleration voltage of 15 kV, a beam current of 40 nA and acquisition times of 20 and 10 s for Fe and S, respectively, whereas traces of Au, Sb and As were counted for 60, 40, and 30 s on peak with 20, 15, and 10 s on protolith (both sides). Natural and synthetic standards were used for calibration and data reduction was performed with PAP software (Pouchou and Pichoir 1991). The detection limits were 220 ppm for Au, 130 ppm for Sb, and 170 ppm for As.

#### Fluid inclusions

Microthermometry analyses were conducted on a US Geological Survey-style (Fluid) gas-flow heating and freezing stage calibrated with synthetic fluid inclusions. Ice-melting and homogenization temperatures are accurate and reproducible to  $\pm 0.2$  and  $\pm 1^\circ\text{C}$ , respectively. Fluid inclusions were studied using the fluid inclusion assemblages concept (Goldstein and Reynolds 1994). Criteria to identify inclusion origin included: (1) primary inclusions were identified by their presence on mineral growth zones; (2) secondary inclusions occur in planar arrays; (3) pseudosecondary inclusions occur in healed fractures that terminate within a crystal, and (4) all other inclusions were assigned an unknown origin.

#### Isotope geochemistry

Powdered samples of host-rock carbonates and vein calcite were obtained by micro drilling. The  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values were determined at the Delta-Lab of the Geological Survey of Canada (Québec), following the method of Al-Aasm et al. (1990).  $\delta^{18}\text{O}$  values of quartz were determined at the Stable isotope laboratory of University Laval (Québec) following the method of Clayton and Mayeda (1963). Data

are reported in the usual ‘per mil’ (‰) notation relative to the standard Vienna Pee Dee belemnite (VPDB; C) and Vienna Standard Mean Ocean Water (VSMOW; O). Precision of data is always better than 0.1‰ for both  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  in carbonates and 0.2‰ in quartz. Accuracy is good, as determined by analysis of NBS-28 (quartz), NBS-18, NBS-19, CO1 and CO9 (carbonates).

#### Petrography of Au-Sb-As mineralization at SAR

The mineralization consists of two subvertical, Au-Sb-As-mineralized extensional quartz-carbonate-sulfide veins cutting across a meter-wide quartz±As-Sb-rich stockwork zone. They are hosted by Silurian laminated silty and argillaceous silicified limestone of the White Head Formation (Fig. 2). The main vein (No. 1; Fig. 3) is subvertical, 30 m long and 10–50 cm thick (Fig. 3; Wares 1990; Pelchat 1995). This vein averages 6.0 g/t Au (highest grade 39.6 g/t Au) and 2.43% Sb (Dessureault 1990). Vein No. 2 is located 75 m northeast of vein No. 1 and is 30 cm thick and 100 m long. It shows strong brecciation and consists of quartz, stibnite, and arsenopyrite hosted by argillaceous nonsilicified limestone (Dessureault 1990). All the data presented in this study come from vein No. 1.

#### Mineral paragenesis

The vein comprises 40–50% of drusy quartz (0.1–3 mm long), 10–15% of sparry calcite crystals, or millimetric to centimetric angular fragments of the host-rock, and 30–35% of sulfides, mostly stibnite with minor arsenopyrite and pyrite. Open spaces filling textures are locally present within the vein where 5–10-mm long quartz crystals are perpendicular to the walls. Prismatic stibnite crystals are 1–2 mm long and grew perpendicular to the vein wall and are usually better developed in the center of the vein. Arsenopyrite crystals are also perpendicular to the walls and are concentrated along the margins of the vein (Pelchat 1995). They represent 5% of the vein and occur as tabular aggregates up to 20  $\mu\text{m}$  long, forming inclusions in quartz and stibnite. The host-rock fragments contain arsenopyrite and framboidal pyrite, probably of diagenetic origin. Dessureault (1990) reported gudmundite ( $\text{FeSbS}$ ) associated with stibnite, but it was not observed in this study. Kaolinite accounts for 1–2% of the vein. It fills interstices between quartz crystals, and it also occurs in limestone fragments.

The host limestone is silicified up to 2.5 m wide along the contact with the vein with locally massive silica replacement. A stockwork zone (1–2 m thick) of quartz-calcite veinlets is also developed in the host limestone. Most of the veinlets are northwest trending, subparallel to the main vein (Fig. 3), and the minor ones are northeast

trending, bedding parallel and perpendicular to the main vein (Fig. 3). Quartz crystals in northwest-trending veinlets are usually perpendicular to the walls. The silicified limestone contains up to 90% quartz with kaolinite, arsenopyrite, and pyrite (1–5%). Pyrite is mostly located along stratification planes in silty laminations. Within the silicified limestone, veinlets are made up of quartz. At a greater distance from the vein, silicification is less developed and the host rock suffered a late carbonatization. It is made up of 95% calcite, 2% quartz and 1% pyrite and arsenopyrite, with 5–10% of the carbonates in late calcite veinlets. In some samples, carbonate veinlets cut across quartz veinlets, clearly indicating that at least part of the carbonatization occurred after silicification. In addition, some veins show evidence of euhedral quartz crystals replaced by calcite. In both the silicified and carbonatized zones, pyrite is present as framboids and as idiomorphic grains. These idiomorphic grains may be of diagenetic or hydrothermal origin. Most of the idiomorphic grains are rimmed by arsenian pyrite (Fig. 4).

Careful SEM observations did not reveal the presence of microscopic gold grains in vein quartz and sulfides. EPMA shows that (1) Au is contained, in altered host rocks, in arsenian pyrite overgrowth on subidiomorphic pyrite; (2) in vein, Au is contained in arsenopyrite as well as in arsenian pyrite overgrowth on framboidal pyrite contained in host-rock fragments; and (3) the arsenian-rich overgrowths are also enriched in Sb. The paragenetic relationship among minerals is described in Fig. 5.

#### Hydrothermal clay mineral assemblages

X-ray diffraction analyses of insoluble residues from White Head limestones show that the mineralogical assemblages vary according to their proximity to faults or mineralized showings (Fig. 6). In addition to the unaltered clay assemblage, five alteration assemblages are defined by an index mineral or by abnormal proportions of illite or chlorite. The proportion of feldspar is variable and does not show any variation with other minerals or with the location of the sample.

*Normal (protolith, unaltered)* The less than 2  $\mu\text{m}$  fraction of the unaltered or “normal” assemblage comprises the following: illite, chlorite, quartz, and rare Na-feldspar and/or K-feldspar. Illite and chlorite are well crystallized, illite to chlorite ratio is around 70:30. Kübler’s illite crystallinity index (Kübler 1968) indicates anchi-epimetamorphic zones (Fig. 7). Moreover, peak intensity ratios indicate that illite belongs to the muscovite–phengite type and that chlorite is mainly magnesian (Chagnon 1988; Chagnon and Desjardins 1991). About 50% of the samples belong to this assemblage.

*Illite assemblage* This assemblage contains mainly illite with some quartz and sometimes traces of feldspar, chlorite and illite/smectite mixed-layer minerals. As seen in Esquevin’s diagram (Fig. 7; Esquevin 1969), illite in this assemblage shows, generally, a more trioctahedral character than illite from other assemblages.

*Kaolinite assemblage* In this assemblage, kaolinite is accompanied by illite, quartz, and traces of feldspar. Only two occurrences of chlorite were observed in this assemblage. As shown by the 001/002 XRD reflection intensity ratio, the composition of illite is the same as in the unaltered assemblage (Esquevin’s diagram; Fig. 7). However, some samples show a low 002/001 XRD reflection intensity ratio that is typical of the illite assemblage.

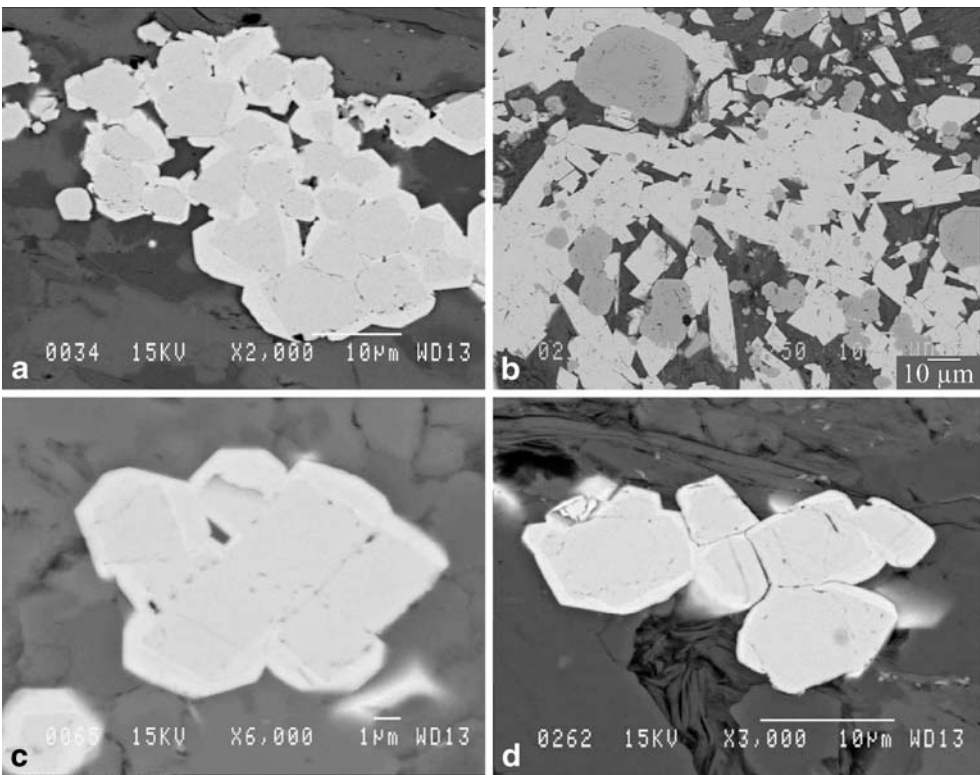
*Smectite assemblage* This assemblage contains illite as the major mineral with smectite and minor chlorite, quartz, and feldspar. The crystallinity of illite is similar to that of the unaltered assemblage.

*Kaolinite + smectite assemblage* Presence of both kaolinite and smectite characterizes this assemblage, where illite is always present with quartz and trace feldspar. Illite in this assemblage shows the crystallinity of illite in the unaltered assemblage.

*Chlorite assemblage* Chlorite is more abundant than illite. No other phyllosilicate is usually present. Quartz and rare feldspar are detected.

*Distribution of the assemblages* As shown in Fig. 6, the alteration assemblages form zoned halos or single spots. In the SAR area, two skarn zones are surrounded by zoned clay halos (1; Fig. 6). The skarn is characterized and surrounded by a chlorite zone assemblage that is in turn surrounded by smectite, kaolinite+smectite, kaolinite, and illite zones. The larger halo (1, 2; Fig. 6) is truncated by the Restigouche fault. Elsewhere, clay halos do not always contain all the assemblages. Eastward from the first two, a halo is found along the Restigouche fault without the skarn and the chlorite zone (3; Fig. 6). This is also the case in the southern part of the area along the Kempt West and Mill brooks (4; Fig. 6) and, further to the northeast, around the Basket Brook and St-Fidèle copper showings (5; Fig. 6). In this latter area, the chlorite assemblage is found, but skarn was not observed. Halos of clay mineral alteration assemblages are found adjacent or close to major faults. The SAR halo is crosscut by the Restigouche fault and no evidence for alteration is detected in rocks of the Fortin Group, north of the fault (Fig. 6; Duba and Williams-Jones 1983; Héroux and Chagnon 1986). Halos to the south are

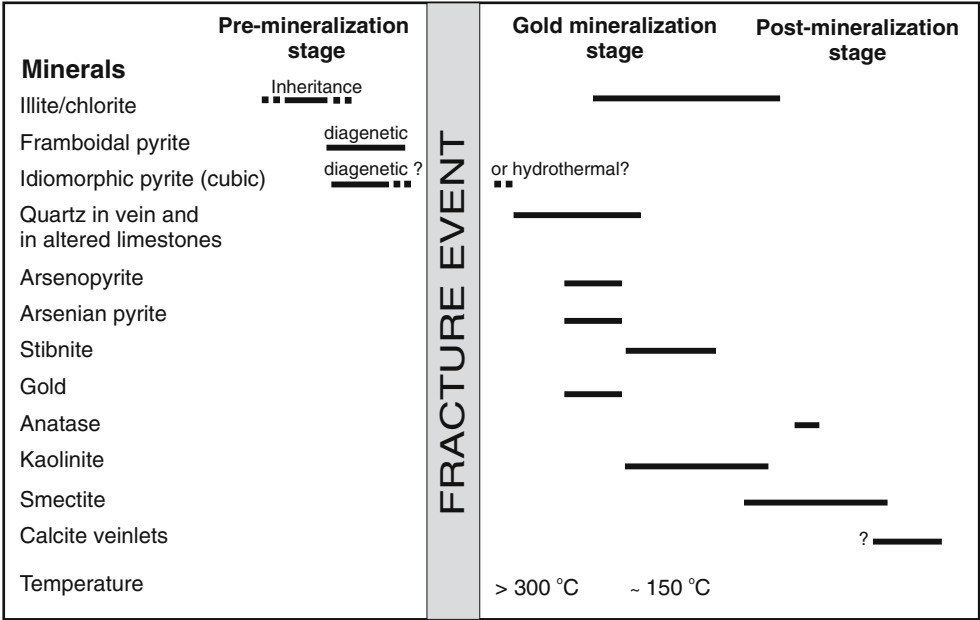
**Fig. 4** **a, c, d** SEM-BSE images of pre-ore pyrite cores (*medium gray*) surrounded by arsenic- and gold-bearing overgrowths (*white*), in silicified calcilutite. Samples CP-T02-4, CP-T19, and CP-T18-4, respectively. **b** SEM-BSE images of pre-ore pyrite cores (*dark gray*) surrounded by arsenic- and gold-bearing overgrowths (*medium gray*) with arsenopyrite (*white*) in a calcilutite fragment contained in the main quartz vein (sample CP-T13-3)



located north of the Sellarsville fault and no sign of alteration was detected south of the fault (Fig. 6).

*Alteration clay assemblages and mineralized showings*  
Four occurrences of copper mineralization are found in this area. All of them are associated with skarns and with the chlorite assemblage. The SAR-Au showing is found within the kaolinite assemblage, very close to the kaolinite-smectite assemblage.

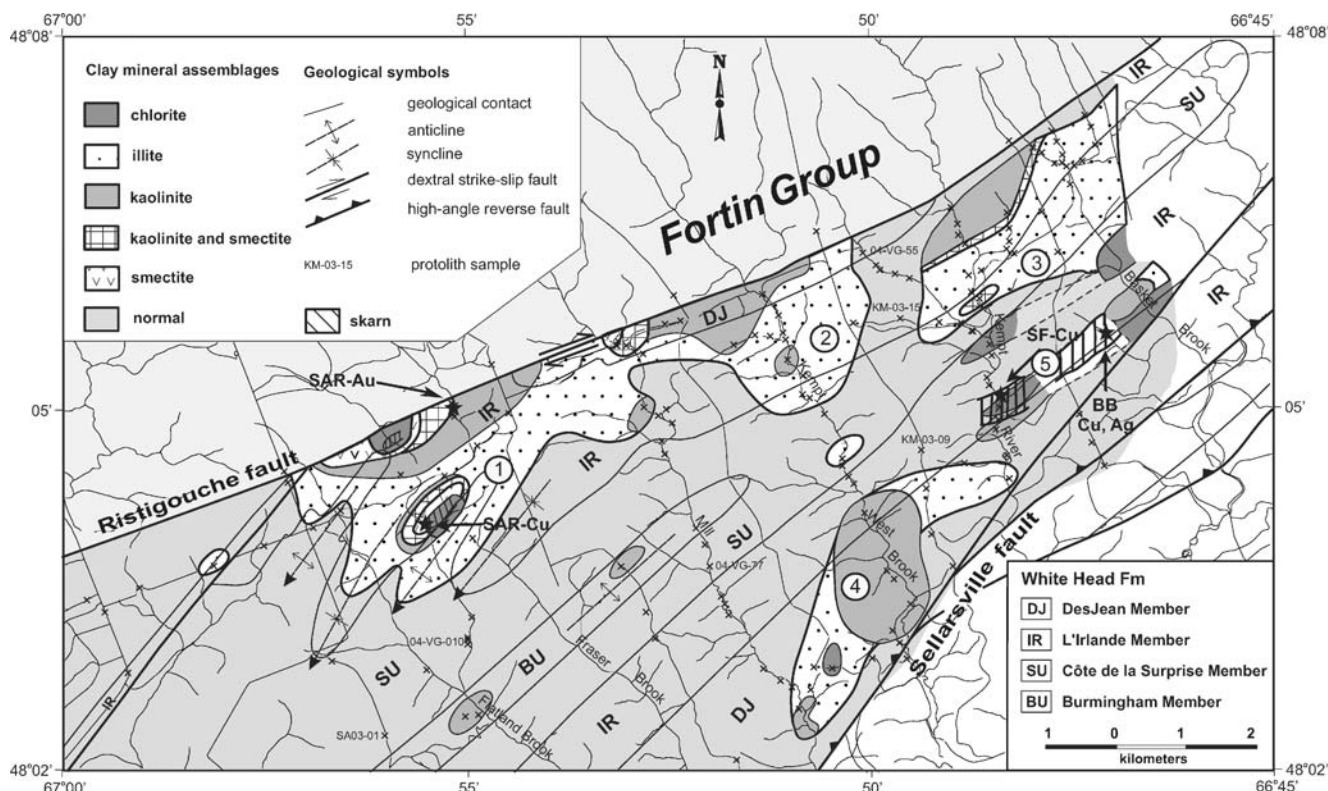
**Fig. 5** Paragenesis of minerals in pre-, syn-, and post-gold mineralization stages



**Geochemistry**

**Whole-rock analyses**

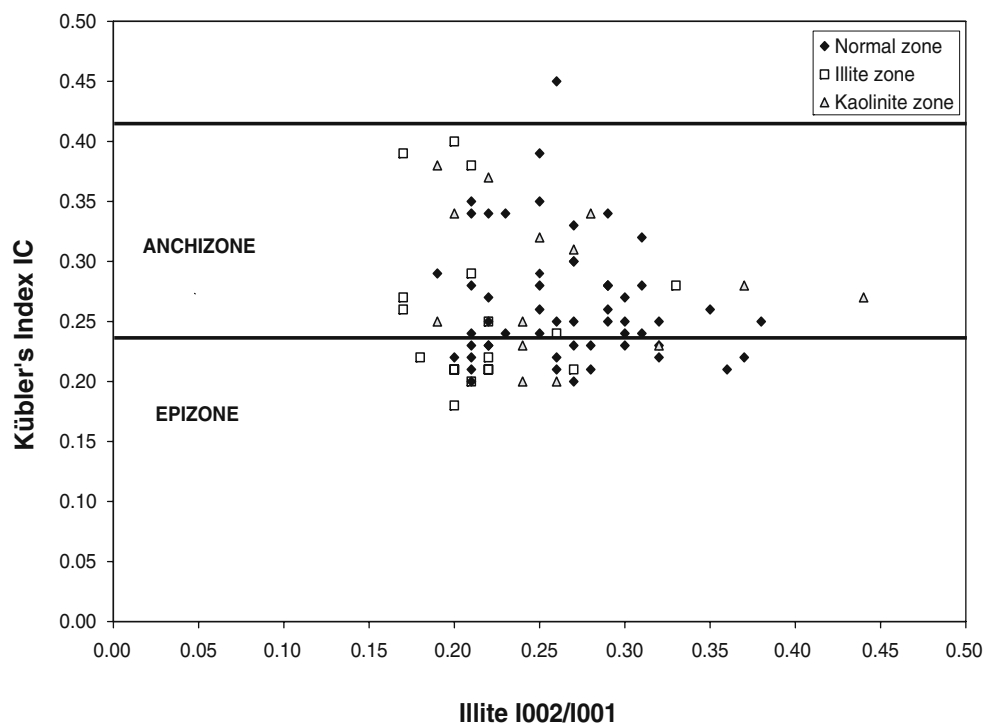
Major, minor, and trace element concentrations, in silicified and carbonatized rocks were determined to identify elemental gain/losses associated with mineralization and alteration (Tables 1 and 2; Fig. 3). Au is not only contained in the Au-Sb-quartz vein, but it is also present in the



**Fig. 6** Alteration map of southwestern Gaspé area near the SAR-Au showing based on clay mineral assemblages (modified from Chagnon 1984). Crosses correspond to the samples collected during summers 2003 and 2004. BB, Cu–Ag indicate Basket Brook Cu–Ag showing;

SAR-Au indicate Saint-André-de-Restigouche Au showing; SAR-Cu indicate Saint-André-de-Restigouche Cu showing; SF-Cu indicate Saint-Fidèle Cu showing

**Fig. 7** Esquevin's diagram for illite from the normal, illite, and kaolinite zones



**Table 1** Chemical analyses of samples from the main quartz vein, the silicified zone and the carbonatised zone at SAR-Au showing main vein, and from the protolith

| Sample            | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | CaO   | MgO  | Na <sub>2</sub> O | K <sub>2</sub> O | Fe <sub>2</sub> O <sub>3</sub> * | MnO   | TiO <sub>2</sub> | P <sub>2</sub> O <sub>5</sub> | Cr <sub>2</sub> O <sub>3</sub> | LOI   | Total  |
|-------------------|------------------|--------------------------------|-------|------|-------------------|------------------|----------------------------------|-------|------------------|-------------------------------|--------------------------------|-------|--------|
| Au-Sb-quartz vein |                  |                                |       |      |                   |                  |                                  |       |                  |                               |                                |       |        |
| 04-MM-005-C7B     | 91.91            | 3.75                           | 0.47  | 0.19 | <0.01             | 0.25             | 1.24                             | <0.01 | 0.23             | 0.04                          | <0.01                          | 1.85  | 99.94  |
| CP-T09-1          | 90.29            | 2.39                           | 0.68  | 0.42 | <0.01             | 0.18             | 1.80                             | 0.01  | 0.13             | 0.01                          | 0.06                           | 1.75  | 97.75  |
| Silicified zone   |                  |                                |       |      |                   |                  |                                  |       |                  |                               |                                |       |        |
| 04-MM-005-C7C     | 87.65            | 4.01                           | 2.19  | 0.93 | <0.01             | 0.40             | 0.90                             | 0.01  | 0.20             | 0.04                          | <0.01                          | 3.75  | 100.10 |
| 04-MM-005-C7D     | 78.70            | 5.08                           | 4.82  | 2.09 | <0.01             | 0.47             | 1.41                             | 0.03  | 0.27             | 0.05                          | <0.01                          | 7.35  | 100.30 |
| 04-MM-005-C7E     | 61.96            | 7.65                           | 9.30  | 3.77 | <0.01             | 1.11             | 3.18                             | 0.05  | 0.41             | 0.10                          | 0.01                           | 12.60 | 100.20 |
| 04-MM-005-C7F     | 82.31            | 5.42                           | 3.59  | 1.39 | <0.01             | 0.48             | 1.29                             | 0.02  | 0.27             | 0.06                          | <0.01                          | 5.55  | 100.40 |
| 04-MM-005-C7G     | 66.39            | 7.04                           | 8.74  | 2.37 | <0.01             | 0.87             | 3.03                             | 0.04  | 0.35             | 0.08                          | <0.01                          | 10.40 | 99.37  |
| CP-T-18           | 77.46            | 6.86                           | 4.25  | 1.86 | <0.01             | 0.80             | 1.72                             | 0.03  | 0.32             | 0.06                          | 0.02                           | 6.80  | 100.20 |
| CP-T-07           | 84.63            | 4.42                           | 2.73  | 0.92 | <0.01             | 0.29             | 1.01                             | 0.03  | 0.18             | 0.06                          | <0.01                          | 5.08  | 99.38  |
| CP-T11            | 76.17            | 7.66                           | 2.03  | 1.19 | <0.01             | 0.90             | 3.59                             | 0.02  | 0.38             | 0.06                          | 0.03                           | 4.10  | 96.16  |
| Carbonatized zone |                  |                                |       |      |                   |                  |                                  |       |                  |                               |                                |       |        |
| 04-MM-005-C9A     | 14.08            | 3.81                           | 41.81 | 1.27 | 0.04              | 0.86             | 1.75                             | 0.04  | 0.19             | 0.04                          | <0.01                          | 35.30 | 99.35  |
| 04-MM-005-C9B     | 17.14            | 5.40                           | 36.79 | 2.99 | 0.04              | 1.41             | 2.52                             | 0.05  | 0.27             | 0.05                          | <0.01                          | 32.95 | 99.78  |
| CP-T03            | 66.42            | 5.28                           | 11.61 | 1.64 | 0.04              | 0.87             | 2.11                             | 0.06  | 0.26             | 0.09                          | <0.01                          | 11.30 | 99.73  |
| CP-T05            | 18.15            | 4.46                           | 37.87 | 2.97 | 0.07              | 0.98             | 2.00                             | 0.04  | 0.21             | 0.04                          | <0.01                          | 33.35 | 100.30 |
| CP-T-25           | 21.36            | 1.85                           | 40.49 | 0.96 | 0.03              | 0.30             | 1.17                             | 0.04  | 0.08             | 0.02                          | <0.01                          | 32.95 | 99.45  |
| CP-T-15           | 74.07            | 4.68                           | 7.13  | 2.42 | <0.01             | 0.82             | 1.90                             | 0.05  | 0.24             | 0.08                          | 0.01                           | 8.75  | 100.20 |
| CP-T-08           | 82.73            | 1.38                           | 8.38  | 0.22 | <0.01             | 0.20             | 0.58                             | 0.02  | 0.10             | <0.01                         | <0.01                          | 6.55  | 100.20 |
| Protolith         |                  |                                |       |      |                   |                  |                                  |       |                  |                               |                                |       |        |
| SA-03-001         | 20.41            | 5.02                           | 35.49 | 2.88 | 0.56              | 1.14             | 2.54                             | 0.05  | 0.25             | 0.04                          | <0.01                          | 31.20 | 99.71  |
| KM-03-015         | 9.09             | 2.17                           | 46.07 | 1.30 | 0.20              | 0.38             | 0.99                             | 0.02  | 0.11             | 0.01                          | <0.01                          | 38.15 | 98.64  |
| 04-VG-010         | 34.12            | 8.37                           | 23.80 | 3.78 | 0.99              | 1.64             | 4.18                             | 0.09  | 0.46             | 0.08                          | 0.02                           | 22.70 | 100.40 |
| 04-VG-077         | 27.54            | 5.51                           | 33.00 | 1.91 | 0.81              | 0.96             | 2.74                             | 0.08  | 0.30             | 0.04                          | 0.01                           | 27.50 | 100.50 |
| 04-VG-055         | 21.36            | 6.43                           | 35.16 | 1.88 | 0.41              | 1.17             | 2.92                             | 0.08  | 0.32             | 0.05                          | <0.01                          | 30.35 | 100.20 |
| KM03-009          | 11.98            | 2.11                           | 44.87 | 1.17 | 0.38              | 0.30             | 0.98                             | 0.04  | 0.10             | 0.02                          | <0.01                          | 36.85 | 98.92  |

All samples in wt. %

&lt;, below detection limit

\*total Fe as Fe<sub>2</sub>O<sub>3</sub>\*

silicified and carbonatized country rocks, where Au grades reach up to 2 g/t and 0.962 g/t, respectively.

Element immobility and mobility can be identified using diagrams that show the concentration of one element in an altered vs a fresh sample (protolith). In these plots, immobile elements form a straight line that passes through the origin (Finlow-Bates and Stumpfl 1981; Grant 1986; Cail and Cline 2001) reflecting no mass change for these elements. A plot of SAR-Au showing TiO<sub>2</sub> vs Al<sub>2</sub>O<sub>3</sub> produces a linear regression that passes through the origin with a  $r^2$  of 0.97 (Fig. 8). The same covariation is also observed between V and Al ( $r^2=0.95$ ) and between Zr and Al ( $r^2=0.94$ ). These high  $r^2$  values indicate immobile behavior for these elements in the altered sedimentary rocks of the SAR-Au showing, and they will be used to define the isocon (Fig. 9).

The composition of the protolith is estimated as the average of samples SA-03-001 and 04-VG-010 (Tables 1 and 2). The slope of the isocon represents the ratio of rock mass before alteration to rock mass after alteration (Grant 1986). The isocon is the line defined by Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Zr, and V (Fig. 9a–d). At the SAR-Au showing, the change in

mass of the altered host rock varies from one sample to another, but elemental gains/losses are coherent between samples showing the same type of alteration. The isocon diagrams for samples from silicified alteration show enrichment in SiO<sub>2</sub>, As, Sb, Au, and Hg and depletion in CaO, Mn, Fe, Cr, and Ag. Base metals exhibit erratic behavior, with minor enrichments and depletions (Fig. 9a,b; full diamonds). The silicification may be very intense, SiO<sub>2</sub> reaching up to 80 wt. % in some samples (Table 1; silicified zone). The altered rocks can be compared to replacement jasperoids typical of Carlin-type deposits and containing episodically silicified breccias, quartz vein stockworks, elevated As, Sb, Hg, Ba, and Tl, and locally anomalous Au and Ag (Nelson 1990; Table 2). Silicification is developed on 1–3 m on the eastern flank of the main vein No. 1, whereas carbonatization is developed for almost 2 m away from the selvages of the vein (Fig. 3). Samples from carbonatized alteration show enrichment in As, Sb, Au, and Hg (Fig. 9c,d). SiO<sub>2</sub> is enriched in some samples (Fig. 9d) but exhibits no significant change in concentration in other samples (Fig. 9c), whereas CaO exhibit minor erratic

**Table 2** Metallic signature of the SAR-Au showing main vein and from the background

| Samples                  | Au<br>(ppb) | As<br>(ppm) | Sb (ppm) | Hg<br>(ppb) | Te<br>(ppm) | Tl<br>(ppm) | Ba<br>(ppm) | Cu<br>(ppm) | Zn<br>(ppm) | Pb<br>(ppm) | Ag<br>(ppm) |
|--------------------------|-------------|-------------|----------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| <b>Au-Sb-quartz vein</b> |             |             |          |             |             |             |             |             |             |             |             |
| CP-T04 (veinlet)         | 295         | 405         | >100000  | 623         | <0.1        | 0.3         | 2           | 6.3         | 2.6         | <2          | <0.2        |
| CP-T09                   | >2000       | 7830        | 873      | 688         |             |             | 22          | 14.5        | 39.6        | 5           | 0.2         |
| CP-T13-2_TR3             | 10660       | 5460        | 5210     | 113         | 0.5         | <0.1        | 13          | 15.5        | 7.9         | 4           | <0.2        |
| 04-MM-005-C7A            | 627         | 1400        | >100000  | 635         | 0.3         | 0.2         | 4           | 13.1        | 3.3         | <2          | <0.2        |
| 04-MM-005-C7B            | 11380       | 4530        | 4590     | 285         | 0.5         | <0.1        | 64          | 15.9        | 31.1        | 7           | 0.2         |
| <b>Silicified zone</b>   |             |             |          |             |             |             |             |             |             |             |             |
| CP-T-07                  | 744         | 990         | 162      | 100         | 0.2         | <0.1        | 47          | 4.4         | 18.7        | <2          | 0.2         |
| CP-T11                   | >2000       | >10000      | 74       | 519         |             |             | 95          | 23.3        | 55.2        | 5           | 0.2         |
| 92-CP-T-18               | 517         | 478         | 282      | 162         | 0.3         | 0.2         | 90          | 10.3        | 51.2        | <2          | 0.4         |
| 92-CP-T-19               | 557         | 1210        | 148      | 128         | 0.3         | 0.2         | 106         | 12.5        | 42.5        | <2          | 0.4         |
| 92-CP-T-20               | 519         | 895         | 1270     | 46          | 0.3         | <0.1        | 56          | 6.2         | 16.9        | <2          | 0.2         |
| 92-CP-T-22               | 18          | 1680        | 144      | 90          | <0.1        | 0.2         | 116         | 7.6         | 27.3        | <2          | 0.5         |
| 04-MM-005-C7C            | 897         | 831         | 169      | 121         | 0.1         | <0.1        | 59          | 10.2        | 39.9        | 2           | 0.2         |
| 04-MM-005-C7D            | 216         | 307         | 148      | 173         | 0.1         | <0.1        | 66          | 16.8        | 54.1        | 3           | 0.4         |
| 04-MM-005-C7E            | 155         | 397         | 198      | 201         | 0.2         | 0.2         | 124         | 14.1        | 52.7        | 5           | 0.4         |
| 04-MM-005-C7F            | 449         | 733         | 112      | 141         | 0.3         | <0.1        | 62          | 14.7        | 35.8        | 3           | 0.3         |
| 04-MM-005-C7G            | 360         | 670         | 451      | 215         | 0.2         | 0.2         | 114         | 17.6        | 57.3        | 5           | 0.5         |
| <b>Carbonatized zone</b> |             |             |          |             |             |             |             |             |             |             |             |
| CP-T-08                  | 28          | 122         | 503      | 49          | 0.3         | <0.1        | 25          | 16.5        | 11.1        | <2          | 0.3         |
| CP-T-15                  | 120         | 668         | 95       | 121         | 0.3         | 0.2         | 95          | 5.7         | 31.8        | <2          | 0.3         |
| 92-CP-T-21               | 6           | 309         | 64       | 61          | 0.1         | <0.1        | 66          | 4.9         | 11.6        | <2          | 0.4         |
| 92-CP-T-24               | 962         | 1390        | 256      | 72          | <0.1        | 0.1         | 68          | 7.5         | 23.2        | <2          | 0.3         |
| 92-CP-T-26               | <5          | 94          | <50      | 164         | 0.2         | 0.3         | 185         | 17.6        | 45.8        | 7           | 0.6         |
| 92-CP-T-29               | 5           | 124         | 137      | 112         | <0.1        | 0.2         | 138         | 14.4        | 33.4        | 2           | 0.6         |
| 04-MM-005-C9A            | 14          | 31          | <50      | 58          | <0.1        | 0.2         | 109         | 9.2         | 27.9        | <2          | 0.5         |
| 04-MM-005-C9B            | 6           | <30         | <50      | 88          | 0.2         | 0.2         | 138         | 10.4        | 28.3        | 2           | 0.5         |
| CP-T03                   | 98          | 837         | 502      | 217         |             |             | 99          | 6           | 39.3        | 4           | 0.6         |
| CP-T05                   | 14          | 49          | 8        | 139         |             |             | 110         | 6.9         | 27.9        | 4           | 1.2         |
| <b>Protolith</b>         |             |             |          |             |             |             |             |             |             |             |             |
| KM-03-015                | 10          | 5.2         | <0.5     | <5          | <0.1        | <0.1        | 56          | 7.5         | 16.5        | <2          | 0.3         |
| SA03-001                 | 8           | 3.9         | 5        | 6           | <0.1        | 0.2         | 145         | 12.2        | 30.7        | 3           | 0.6         |
| 04-VG-010                | <5          | 12          | <5       | 29          |             |             | 214         | 12          | 47.7        | 6           | 1.0         |
| 04-VG-077                | <5          | 10          | <5       | 20          |             |             | 128         | 9.4         | 34.4        | 3           | 1.2         |
| 04-VG-055                | <5          | 5.0         | <5       | 13          |             |             | 172         | 11.9        | 38.8        | 5           | 1.2         |
| KM03-009                 | <5          | 4.0         | <5       | 11          |             |             | 41          | 4.8         | 17.9        | <2          | 1.0         |

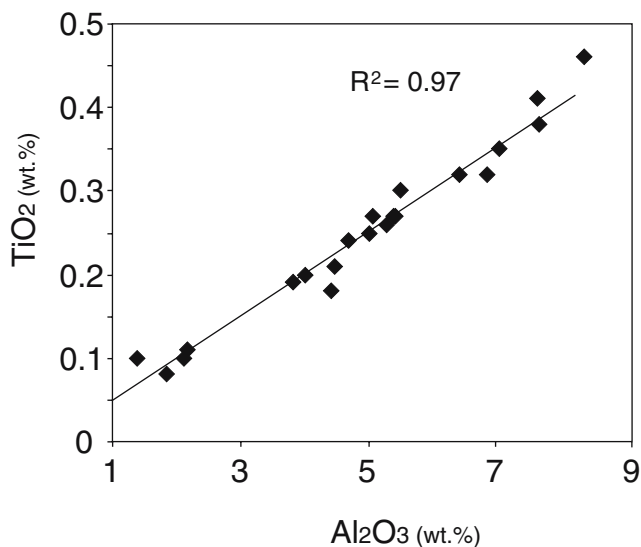
enrichments and depletions (Fig. 9c,d, respectively). However, there is only a small variation in major oxides. This may indicate that the mineralizing fluids were in equilibrium with the host rocks. In addition, Au grades are highest in the most silicified rocks, highlighting a genetic link between the Au-Sb-As-quartz vein and the silicification of Au-bearing surrounding rocks (Tables 1 and 2).

In the silicified zone, Au is positively correlated to As content (Fig. 10a) but not to Sb content (Fig. 10b) suggesting that Au is associated with and possibly hosted by arsenopyrite and/or arsenian pyrite in altered limestones but not with stibnite. There is no correlation between Au and Hg, Cu or Zn. CaO and MgO depletions are consistent with carbonate dissolution during silica replacement. Samples from carbonatized alteration may show enrichment

in CaO, in relation with late replacement of quartz in veinlets by calcite. Depletion in K in the silicified alteration is in agreement with the occurrence of kaolinite associated with gold mineralization at SAR, which results from the removal of K from detrital or diagenetic illite. W content is always below detection limit (10 ppm); Te and Tl contents are also often below detection limits or very low (Table 2).

#### Trace elements in pyrite and arsenopyrite

Trace-element contents in early stage pyrite and late stage pyrite overgrowth, and in arsenopyrite were analyzed by electron microprobe. The overgrowths of arsenian pyrite on early stage pyrite core are usually thinner than 1  $\mu\text{m}$  (Fig. 11a,e), so analyses are often diluted by the surrounding



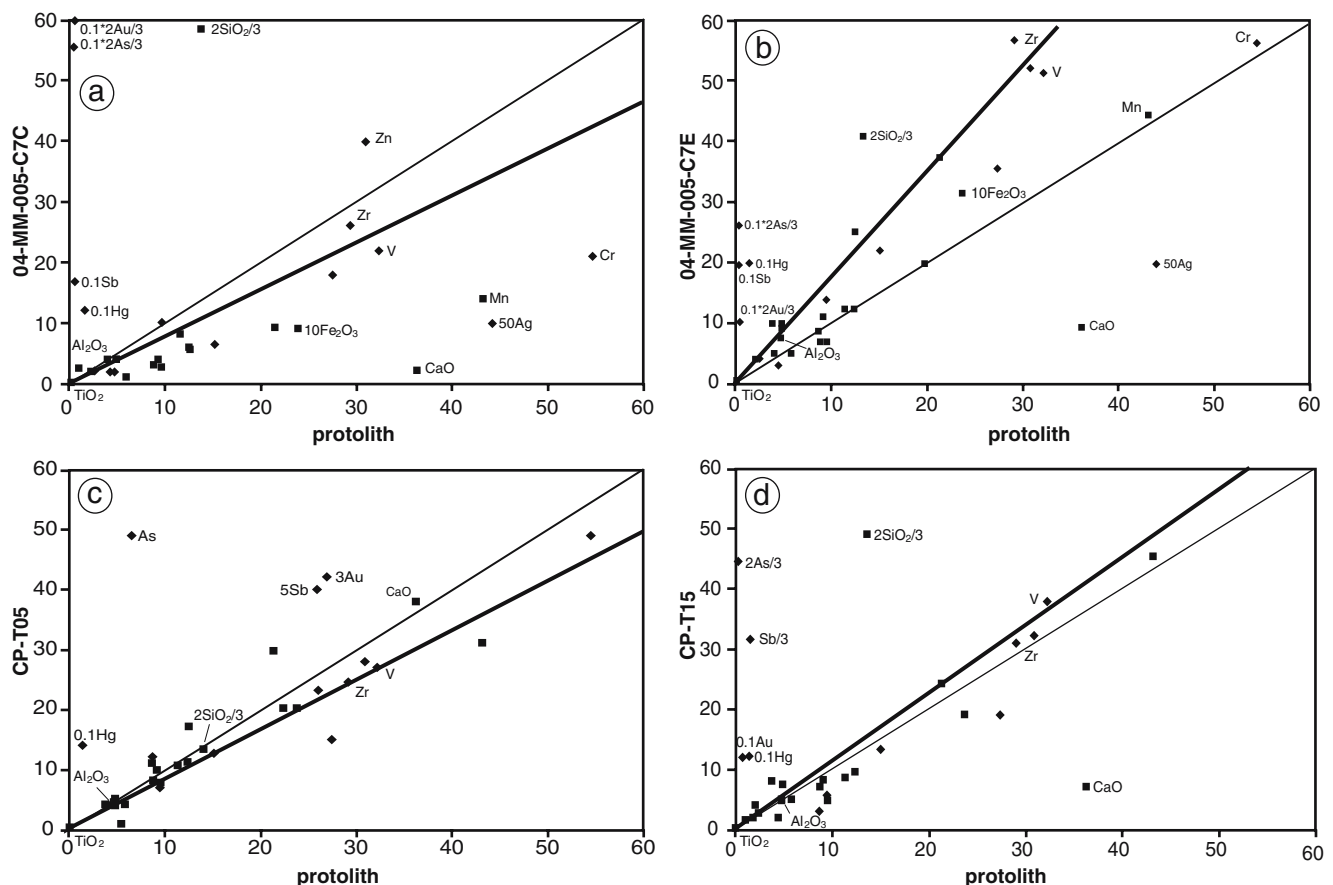
**Fig. 8**  $\text{TiO}_2$  vs  $\text{Al}_2\text{O}_3$  diagram for samples from carbonated and silicified rocks, showing the correlation between both elements

material (early pyrite, carbonate, or quartz). The same dilution may affect core analyses when it is less than  $5\ \mu\text{m}$  thick. Early stage pyrite contains no detectable Au and usually nil to very low As: in most samples, As content in

the core is below 1 wt. %, although in some As-rich samples, it may reach up to 3.9 wt. %, and low Sb (below 1,100 ppm), whereas late pyrite overgrowths are enriched in these elements: up to 15 wt. %, 2,280 ppm, and 2,850 ppm respectively for As, Au and Sb (Table 3, Fig. 11d,g). Most arsenopyrite contains up to 2,250 ppm Au and between 300 and 2,370 ppm Sb (Table 4; Fig. 11d,g). Sb in pyrite overgrowths and in arsenopyrite in quartz veins and veinlets support the hypothesis that the quartz-Au-Sb-As vein, silicification of the host rocks and Au-bearing arsenic-rich pyrite overgrowths were probably deposited by the same mineralizing fluid (Fig. 5). If the pyrite cores in silicified alteration are hydrothermal, their relatively low abundance in Au, As, and Sb indicate that they probably formed during an event that occurred before or earlier than the circulation of the fluid that has lead to the formation of the quartz-stibnite-Au vein.

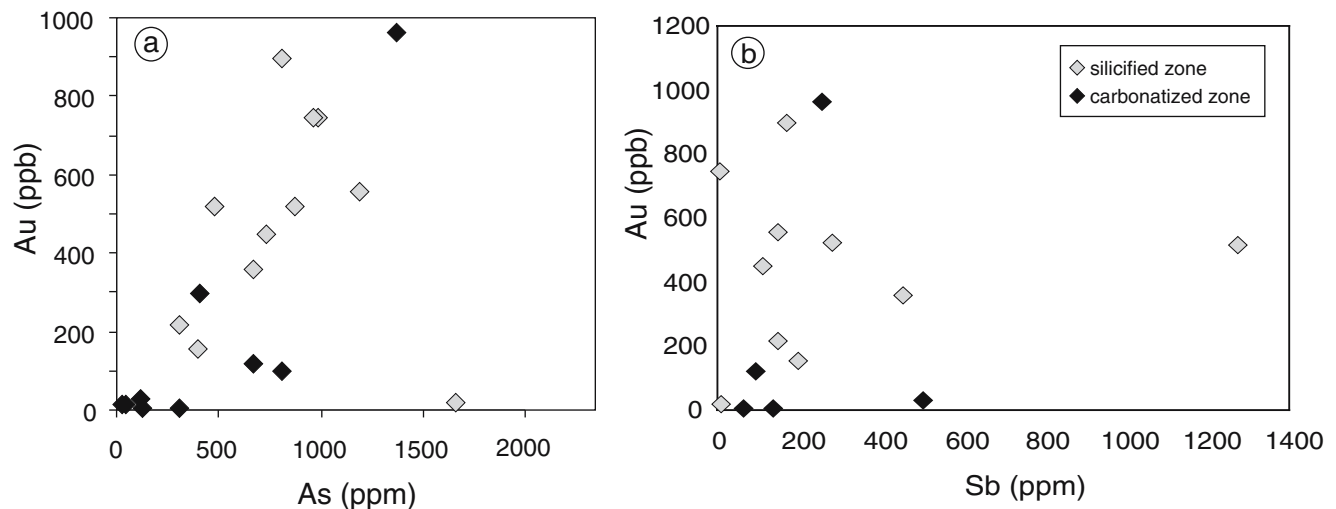
#### Fluid inclusion analysis

Fluid inclusions were analyzed in quartz forming the quartz-carbonate-sulfides No. 1 vein. Quartz from silicified



**Fig. 9** Isocon diagrams for typical samples from the silicified (a and b) and from the carbonated (c and d) zones. On each diagram, the thick line features the isocore drawn through immobile elements (Al, Ti, Zr, V), and the thin line is the line of constant mass. Full diamonds

represent metals and metalloids, full squares for other elements. Data from Tables 1 and 2. Elements that display important gains/losses are labelled. The *protolith* corresponds to the mean values samples SA-03-001 and -04-VG-010 (Tables 1 and 2; see Fig. 6 for location)



**Fig. 10** **a** Au vs As contents and **b** Au vs Sb contents of samples from the SAR-Au showing

limestones contains only few fluid inclusions, which are too small for microthermometry. Fluid inclusions showing variable phase ratio at room temperature and a range of homogenization temperatures in the same fluid inclusions plane were not reported here as they may have suffered post-entrapment modifications.

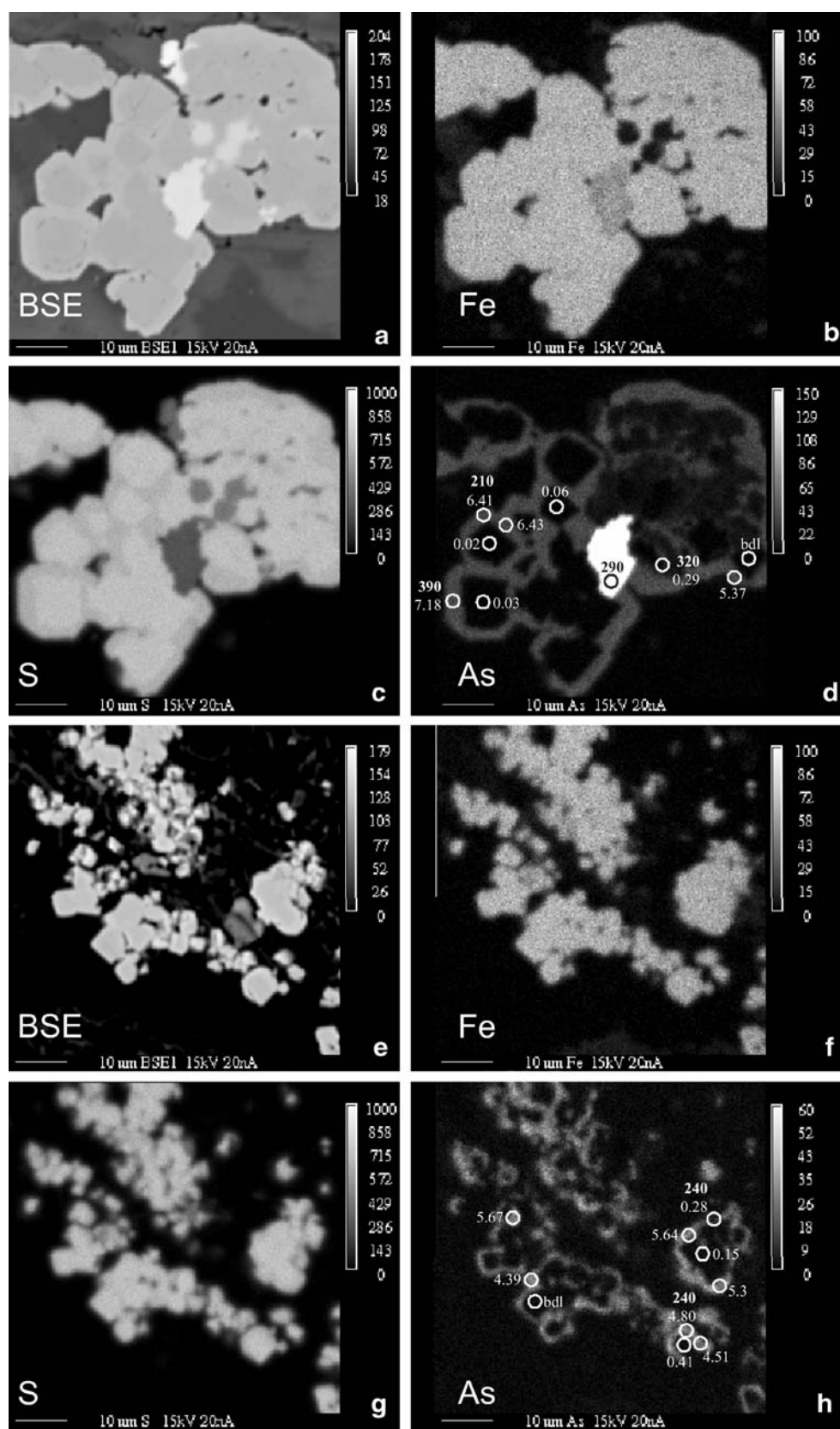
Two types of pseudo-secondary fluid inclusions are distinguished in the quartz vein: (1) Fluid inclusions aligned with the arsenopyrite crystal faces, a few of them along the quartz–arsenopyrite crystals boundary. These inclusions trapped the fluid from which arsenopyrite deposited. All these pseudo-secondary aqueous fluid inclusions are small (generally between 5 and 8  $\mu\text{m}$ ) and contain two-phases with liquid/vapor ratio (L/V ratio) ranging from 10 to 20. They are interpreted to have trapped the mineralizing fluid from which arsenopyrite crystallised. Fluid inclusion analysis (FIA) show homogenization temperatures ranging from 135 to 246°C, with a median of 166°C (Fig. 12) and show salinities between 6.0 and 8.8 wt. % eq. NaCl with a median of 7.2 wt. % eq. NaCl. (2) Other pseudo-secondary fluid inclusion planes, not aligned with arsenopyrite in quartz vein. These fluid inclusions show no obvious relationship to the fluid circulation event that lead to deposition of arsenopyrite and could have trapped fluids that circulated after that event. They are thus considered separately from the previous type. They are also two-phases liquid-rich with L/V ratio between 10 and 20. The FIA show homogenization temperatures ranging from 117 to 277°C, and a median of 170°C. Th distribution is bimodal with peaks at 140–160°C and at 220–260°C. They show salinities between 3.6 and 8.0 wt. % eq. NaCl and a mode at 6.0–7.0 wt. % eq. NaCl (Fig. 12). Two fluid inclusions, one of each type, gave first melting temperatures of 21.0°C, indicating  $\text{H}_2\text{O}$ –NaCl composition for the

fluid. Neither clathrate formation nor  $\text{CO}_2$  melting were observed, indicating that, if present,  $\text{CO}_2$  constitutes less than ~4 mol% of the mineralization fluid (Hedenquist and Henley 1985). Both types of fluid inclusions have similar characteristics but those not linked to the deposition of arsenopyrite exhibit higher homogenisation temperatures. In a temperature of homogenisation (Th) vs salinity diagram, both groups of pseudo-secondary fluid inclusions plot along an inverted “L” pattern (Fig. 13). Fluid inclusions with Th between 150 and 290°C and salinities ranging from 5.0 to 9.0 wt. % eq. NaCl show a range in temperature for constant salinity that is interpreted to document cooling of the fluid. The second trend of the pattern comprises fluid inclusions with Th ranging from 120 to 150°C and salinity from 3.6 to 7 wt. % eq. NaCl, which document dilution of the earlier high-temperature and high-salinity fluid.

#### Carbon and oxygen stable isotopes geochemistry

The oxygen isotope composition of quartz from the SAR quartz-stibnite-sulfides vein and carbon and oxygen isotope composition of silicified and mineralized calcilutites hosting the SAR vein are compared to the C–O isotope composition of unaltered whole-rock calcilutites (Fig. 14; Table 5). Whole-rock unaltered calcilutite has  $\delta^{13}\text{C}_{\text{VPDB}}$  and  $\delta^{18}\text{O}_{\text{VSMOW}}$  values ranging respectively from –0.1 to 1.1‰ and from 20.9 to 23.2‰ for calcite, and respectively from –0.2 to 1.2‰ and from 20.3 to 21.9‰ for dolomite. Silicified and mineralized calcilutites have  $\delta^{13}\text{C}_{\text{VPDB}}$  and  $\delta^{18}\text{O}_{\text{VSMOW}}$  values ranging respectively from –0.1 to 1.2‰ and from 21.3 to 23.6‰ for calcite, and from 0.2 to 1.4‰ and from 22.2 to 23.0‰ for dolomite. The C–O isotope composition of altered rocks is similar to that of unaltered

**Fig. 11** Back-scattered electron images (BSE; **a**) and X-ray map for Fe (**b**), S (**c**), and As (**d**) in pyrite grains from sample CP-T18-2 (silicified zone; *top panel*). BSE (**e**) and X-ray map for Fe (**f**), S (**g**), and As (**h**) in pyrite grains from sample CP-T02-4 (carbonated zone; *bottom panel*). EPMA spots are also indicated with the respective Au (ppm, bold) and As (wt.%) contents. Bdl=below detection limit



**Table 3** Electron microprobe analyses of pyrite cores and their arsenic-rich overgrowths from the SAR-Au showing main vein

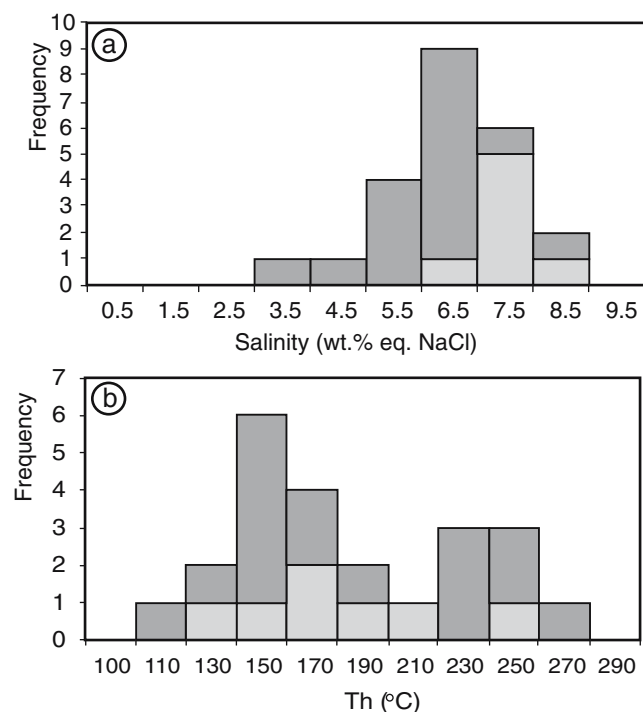
|                      | Sample   | Fe (wt%) | S (wt%) | As (wt%) | Au (ppm) | Sb (ppm) | Total |
|----------------------|----------|----------|---------|----------|----------|----------|-------|
| Pre-ore stage pyrite | CP-T19   | 48.6     | 49.7    | 0.07     | bdl      | 200      | 98.4  |
|                      | CP-T18   | 47.2     | 47.6    | 0.41     | bdl      | 230      |       |
|                      |          | 47.7     | 51.4    | 0.15     | bdl      | 140      | 99.3  |
|                      |          | 48.1     | 51.2    | bdl      | bdl      | bdl      | 99.3  |
|                      | CP-T02-4 | 48.0     | 50.6    | 0.02     | bdl      | bdl      | 98.6  |
|                      |          | 48.0     | 50.2    | 0.03     | bdl      | 250      | 98.2  |
|                      | CP-T05   | 46.7     | 50.4    | 0.58     | bdl      | 180      | 97.7  |
|                      |          | 46.7     | 49.7    | 1.60     | bdl      | bdl      | 98.1  |
|                      | CP-T27   | 47.0     | 50.7    | 0.05     | bdl      | 140      | 97.7  |
|                      |          | 47.1     | 51.2    | 0.03     | bdl      | bdl      | 98.4  |
|                      | CP-T11   | 47.1     | 49.9    | 2.65     | bdl      | bdl      | 99.6  |
|                      |          | 47.2     | 50.3    | 1.84     | bdl      | 170      | 99.3  |
|                      |          | 46.4     | 51.4    | 0.56     | bdl      | 410      | 98.4  |
|                      | CP-T-13  | 46.2     | 49.5    | 1.10     | bdl      | 590      |       |
|                      |          | 48.1     | 51.3    | 0.03     | bdl      | bdl      | 99.4  |
|                      |          | 48.0     | 50.0    | 0.04     | bdl      | bdl      | 98.1  |
|                      |          | 47.8     | 50.7    | bdl      | bdl      | bdl      | 98.5  |
|                      |          | 47.0     | 50.6    | 0.10     | bdl      | 310      | 97.7  |
|                      | CP-T03   | 47.7     | 50.3    | 0.04     | bdl      | 230      | 98.0  |
|                      | CP-T05   | 46.6     | 49.9    | 1.46     | bdl      | bdl      | 98.0  |
|                      |          | 46.6     | 50.8    | 0.48     | bdl      | 550      | 97.9  |
| Ore-stage pyrite     | CP-T19   | 46.5     | 47.4    | 4.47     | 220      | 240      | 98.4  |
|                      | CP-T18   | 45.2     | 45.1    | 4.80     | 240      | bdl      |       |
|                      |          | 47.3     | 50.3    | 0.28     | 240      | bdl      | 97.9  |
|                      | CP-T18   | 46.2     | 50.3    | 0.31     | 2280     | 420      | 97.0  |
|                      |          | 46.0     | 50.3    | 0.98     | 280      | 190      | 97.3  |
|                      | CP-T02-4 | 46.0     | 46.9    | 6.42     | 210      | 830      | 99.0  |
|                      |          | 44.8     | 46.5    | 7.18     | 390      | 960      | 98.6  |
|                      | CP-T05   | 43.4     | 45.4    | 6.67     | 250      | 460      |       |
|                      |          | 43.1     | 44.7    | 7.29     | 220      | 1090     |       |
|                      | CP-T27   | 45.4     | 47.8    | 5.72     | 370      | 150      | 99.0  |
|                      |          | 44.7     | 46.7    | 6.44     | 270      | 160      | 97.9  |
|                      | CP-T11   | 45.4     | 48.0    | 6.03     | 280      | bdl      | 99.4  |
|                      |          | 44.8     | 43.8    | 6.48     | 270      | bdl      |       |
|                      |          | 43.7     | 42.4    | 15.09    | 350      | 220      | 101.2 |
|                      | CP-T13   | 43.8     | 46.0    | 6.06     | 360      | 160      |       |
|                      |          | 45.6     | 45.7    | 6.14     | 330      | 130      | 97.5  |
|                      |          | 45.5     | 45.7    | 8.91     | 240      | 680      | 100.2 |
|                      |          | 43.7     | 42.4    | 15.09    | 350      | 220      | 101.2 |
|                      |          | 46.8     | 48.8    | 3.72     | 360      | 240      | 99.3  |
|                      |          | 47.3     | 49.9    | 1.93     | 260      | 190      | 99.1  |
|                      |          | 45.3     | 45.8    | 5.63     | 260      | 250      |       |
|                      | CP-T05   | 46.5     | 41.0    | 0.37     | 280      | 280      |       |
|                      |          | 46.6     | 40.6    | 5.22     | 1050     | 2480     |       |
|                      |          | 43.0     | 43.6    | 5.42     | 220      | 500      |       |

country rocks (Fig. 14). These values are typical of Ordovician marine carbonates ( $\delta^{13}\text{C} = -2.5$  to  $7\text{‰}$  and  $\delta^{18}\text{O} = 20.1$  to  $29.4\text{‰}$ ; Qing and Veizer 1994). The  $\delta^{18}\text{O}_{\text{VSMOW}}$  values of quartz from the SAR vein and quartz veinlets in silicified calcilutite range from  $21.7$  to  $23.7\text{‰}$  (Table 5; Fig. 14). Calcite in late veinlets has  $\delta^{13}\text{C}_{\text{VPDB}}$  and  $\delta^{18}\text{O}_{\text{VSMOW}}$  values ranging from  $-4.3$  to  $1.4\text{‰}$ , and from  $20.3$  to  $22.0\text{‰}$ , respectively. This range is similar to

both unaltered and altered country rocks for oxygen but slightly lower values for carbon indicate a small contribution from a low  $\delta^{13}\text{C}$  source (Table 5, Fig. 14). Late calcite veinlets yield  $\delta^{18}\text{O}$  values similar to the unaltered host rocks but with  $\delta^{13}\text{C}$  values slightly lower (to  $-4.3\text{‰}$ ). As these veins formed late in the paragenetic sequence, it is most likely that they formed at temperatures lower than the main SAR quartz vein. Quartz vein fluid inclusions

**Table 4** Electron microprobe analyses of arsenopyrite from the SAR-Au prospect main vein

|              | Sample   | Fe (wt%) | S (wt%) | As (wt%) | Au (ppm) | Sb (ppm) | Total |
|--------------|----------|----------|---------|----------|----------|----------|-------|
| Arsenopyrite | CP-T07   | 34.5     | 19.1    | 46.1     | 2378     | 414      | 100.0 |
|              |          | 33.9     | 18.3    | 43.9     | 280      | 330      |       |
|              |          | 34.5     | 20.1    | 44.8     | 1270     | 760      | 99.5  |
|              |          | 35.9     | 21.0    | 42.0     | 250      | 680      | 99.0  |
|              |          | 35.9     | 20.9    | 43.8     | bdl      | 2370     | 100.8 |
|              |          | 35.5     | 20.2    | 44.0     | 620      | 2080     | 100.0 |
|              |          | 35.7     | 21.7    | 43.0     | bdl      | 390      | 100.4 |
|              |          | 35.8     | 21.0    | 42.8     | bdl      | 2040     | 99.9  |
|              | CP-T02-4 | 34.7     | 20.7    | 46.9     | 2520     | 620      |       |
|              |          | 35.9     | 20.8    | 44.2     | bdl      | 1120     | 101.0 |
|              |          | 32.3     | 20.2    | 44.4     | bdl      | 660      |       |
|              | CP-T11   | 35.5     | 20.8    | 44.1     | 290      | 1040     | 100.5 |
|              |          | 35.5     | 19.9    | 45.9     | 1260     | 690      | 101.5 |
|              |          | 35.4     | 20.2    | 45.8     | bdl      | 450      | 101.4 |
|              |          | 36.0     | 21.3    | 44.4     | bdl      | 780      | 101.9 |
|              | CP-T13   | 36.1     | 20.4    | 45.1     | 300      | 730      | 101.7 |
|              |          | 36.2     | 21.7    | 43.4     | bdl      | 590      | 101.4 |
|              |          | 36.7     | 21.7    | 42.0     | 370      | 410      | 100.5 |
|              |          | 36.4     | 19.4    | 45.5     | 620      | 400      | 101.4 |
|              |          | 35.5     | 19.2    | 46.0     | 370      | 450      | 100.8 |
|              |          | 35.9     | 19.9    | 45.6     | 490      | 530      | 101.8 |
|              |          | 35.6     | 19.6    | 45.6     | bdl      | 340      | 100.8 |
|              |          | 36.1     | 20.7    | 44.3     | 460      | 990      | 101.1 |
|              | CP-T18   | 35.9     | 20.0    | 44.8     | 500      | 1160     | 100.9 |
|              |          | 36.1     | 20.7    | 43.5     | 350      | 1100     | 100.5 |
|              |          | 35.9     | 20.7    | 45.0     | bdl      | 1730     | 101.8 |
|              |          | 35.1     | 20.8    | 44.7     | bdl      | 990      | 100.7 |



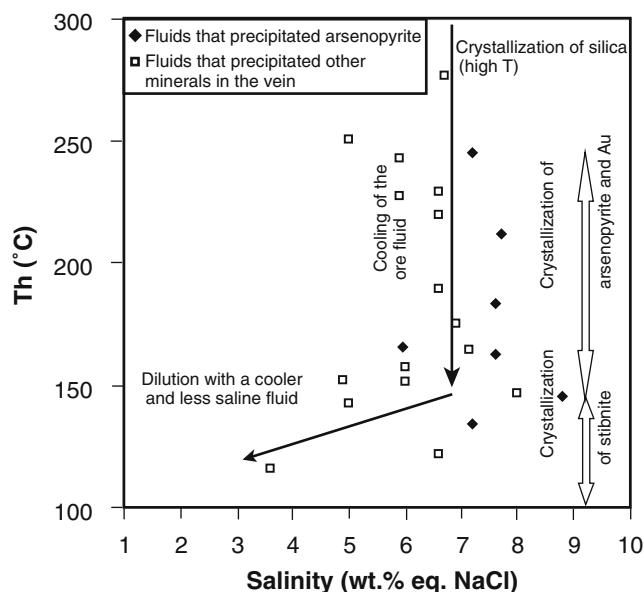
**Fig. 12** Histograms of **a** salinity (wt.% eq. NaCl) and **b** homogenization temperatures (°C) in pseudo-secondary fluid inclusions in quartz from the main vein in SAR-Au showing, corresponding to the mineralizing fluid (*medium gray*) and other fluids (*dark gray*)

suggest that they formed at temperatures as low as 150–100°C.

## Discussion

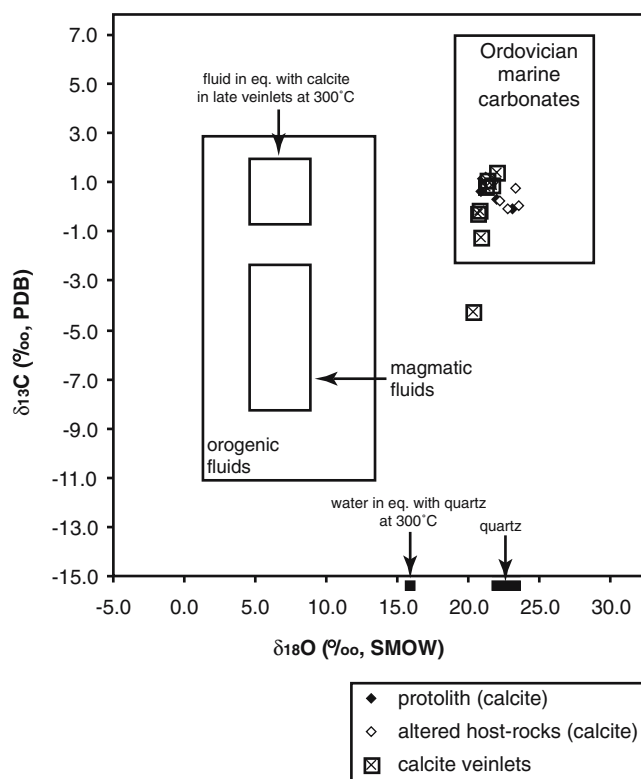
### Tectono-stratigraphic setting during mineralization

A first constraint is represented by the maximal depth of formation of the SAR-Au showing. An estimation of 5–6 km is given by the thickness of Siluro–Devonian units covering the host limestones of the White Head Formation in southwestern Gaspé (Bourque et al. 1993). A second constraint is illustrated by the tectonic regime. The localization of the extensional Au–Sb–As quartz veins at SAR is structurally controlled by the last stage of the Acadian deformation (strike-slip faulting; Malo and Kirkwood 1995) because the veins are found along a releasing bend of the Restigouche fault. The open-space textures of the main vein and the orientation of the stockwork of veinlets parallel to this vein most likely indicate that it is an extension vein compatible with this dextral dilational jog. The depth is probably less than 5.5 km, because the tectonic uplift began during an earlier phase of the Acadian orogeny that preceded



**Fig. 13** Homogenization temperature ( $T_h$ ) vs salinity (wt.% eq. NaCl) diagram for pseudo-secondary fluid inclusions in quartz from the main vein at SAR-Au showing. (22 FIA and 6 samples)

strike-slip faulting (Malo 2001). This latter faulting is post Early Devonian in southwestern Gaspé because rocks of the Fortin Group along the Restigouche fault were affected by



**Fig. 14**  $\delta^{18}\text{O}$  vs  $\delta^{13}\text{C}$  diagram showing the distribution of SAR-Au showing rocks and veins. Boxes corresponding to Ordovician marine carbonates, orogenic fluids, and magmatic fluids are respectively from Qing and Veizer (1994), Hofstra and Cline (2000) and from Sheppard (1986) and Valley (1986)

this strike-slip faulting (Fig. 6). Conglomerates from the Lagarde Formation, in southwestern Gaspé, contain fragments of the White Head Formation, indicating that the White Head limestones were in fact already in part emerged in the late Early Devonian.

#### Origin and evolution of clay mineral assemblages

The original terrigenous assemblage found in the White Head limestones was most likely formed of quartz, illite, chlorite, and feldspars with perhaps some illite/smectite mixed-layer minerals (Chagnon 1988). This original assemblage was subjected to burial metamorphism, which transformed illite/smectite to illite and increased the crystallinity degree of illite and chlorite as well as increased the reflectance of organic matter (Héroux and Chagnon 1986; Chagnon 1988). These two diagenetic indicators show that the sedimentary rocks in the SAR area have reached the anchimetamorphic–epimetamorphic levels. Even if they had been present at the time of sedimentation, kaolinite and smectite should have been recrystallized at such high temperatures (Héroux et al. 1979; Hoffman and Hower 1979; Kübler 1984). Because kaolinite and smectite are present in the insoluble residue of the White Head limestones, they should have formed after the maximum heating related to burial diagenesis, or to hydrothermal activity. Persistence of kaolinite and smectite also indicates that no significant heating occurred after their formation. The chlorite assemblage is very closely associated with skarns and was probably formed by reaction of the wall rock with magmatic fluids that produced the skarns. The smectite assemblage that generally surrounds the chlorite zone could have formed by alteration of chlorite by a later fluid, possibly after the the formation of the SAR-Au showing that is found within a kaolinite assemblage zone. The formation of smectite is most probably the last alteration episode that occurred in that system. The chronology of formation of kaolinite, kaolinite+smectite, and illite assemblages as well as fluid circulation patterns that formed the clay assemblages are difficult to establish. First, the chlorite is generally absent or in very small proportion in those assemblages, such that a relatively low pH fluid would be necessary to remove the Fe and Mg cations coming from the dissolution of chlorite. This low pH fluid would also have decarbonated the host rocks before silicification and precipitated kaolinite from a Si- and Al-rich fluid. K, Fe, and Mg were leached from the kaolinite zone by the fluid that replaced chlorite. Stability fields of these clay minerals and assemblages are controlled by the temperature and by the activities of such cations as Al, Si, Mg, Fe, K, and H. Activity diagrams in the system  $\text{K}_2\text{O}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  have been produced by Aja et al. (1991). They show that the smectite is very temperature

**Table 5** Carbon and oxygen isotopic composition of calcite and dolomite from the unaltered and from the silicified and mineralized host rocks, and from late calcite veinlets at SAR, and oxygen isotopic

composition of quartz from the main quartz-stibnite-Au vein at SAR and quartz veinlets in the silicified calcilutites

| Sample                                       | calcite                              |                                       | dolomite                             |                                       | quartz vein                           |
|----------------------------------------------|--------------------------------------|---------------------------------------|--------------------------------------|---------------------------------------|---------------------------------------|
|                                              | $\delta^{13}\text{C}(\text{‰, PDB})$ | $\delta^{18}\text{O}(\text{‰, SMOW})$ | $\delta^{13}\text{C}(\text{‰, PDB})$ | $\delta^{18}\text{O}(\text{‰, SMOW})$ | $\delta^{18}\text{O}(\text{‰, SMOW})$ |
| Unaltered calcilutite (protolith)            |                                      |                                       |                                      |                                       |                                       |
| 04-VG-055                                    | 0.3                                  | 22.0                                  | −0.2                                 | 20.3                                  |                                       |
| KM-03-009                                    | −0.1                                 | 23.2                                  | 0.1                                  | 21.9                                  |                                       |
| 04-VG-010                                    | 0.6                                  | 20.9                                  | 0.8                                  | 21.5                                  |                                       |
| SA-03-001                                    | 1.1                                  | 21.0                                  | 1.2                                  | 20.6                                  |                                       |
| Mean                                         | 0.5±0.5                              | 21.8±1.1                              | 0.4±0.6                              | 21.1±0.7                              |                                       |
| Altered (silicified) and mineralized samples |                                      |                                       |                                      |                                       |                                       |
| 04-MM-005-C9B                                | 1.0                                  | 21.7                                  | 1.4                                  | 22.2                                  |                                       |
| 04-MM-005-Ch7E                               | 0.7                                  | 23.3                                  | 1.3                                  | 23.5                                  |                                       |
| 92-CP-T15                                    | 0.1                                  | 23.6                                  | 1.2                                  | 23.1                                  |                                       |
| 91-CP-T11                                    | 0.2                                  | 22.2                                  | 0.2                                  | 22.9                                  | 21.7                                  |
| 91-CP-T07                                    | −0.1                                 | 22.8                                  | 0.8                                  | 23.0                                  | 23.7                                  |
| 91-CP-T02                                    | 1.2                                  | 21.3                                  |                                      |                                       |                                       |
| 91-CP-T18                                    | 0.9                                  | 21.4                                  |                                      |                                       |                                       |
| Mean                                         | 0.6±0.5                              | 22.3±0.9                              | 1.0±0.5                              | 22.9±0.5                              |                                       |
| Main SAR-vein                                |                                      |                                       |                                      |                                       |                                       |
| 91-CP-T13                                    |                                      |                                       |                                      |                                       | 23.1                                  |
| 91-CP-T04                                    |                                      |                                       |                                      |                                       | 22.6                                  |
| Late calcite veinlets                        |                                      |                                       |                                      |                                       |                                       |
| 92-CP-T16                                    | 0.8                                  | 21.2                                  |                                      |                                       |                                       |
| 92-CP-T25                                    | −0.3                                 | 20.6                                  |                                      |                                       |                                       |
| 91-CP-T05                                    | 1.1                                  | 21.4                                  |                                      |                                       |                                       |
| 91-CP-T18                                    | −0.2                                 | 20.8                                  |                                      |                                       |                                       |
| 92-CP-T15                                    | −4.3                                 | 20.3                                  |                                      |                                       |                                       |
| 91-CP-T03                                    | −1.3                                 | 20.8                                  |                                      |                                       |                                       |
| 04-MM-005-C9B                                | 0.9                                  | 21.7                                  |                                      |                                       |                                       |
| 91-CP-T02                                    | 1.4                                  | 22.0                                  |                                      |                                       |                                       |
| Mean                                         | −0.2±1.9                             | 21.1±0.6                              |                                      |                                       |                                       |

dependent and has a very small stability field compared to that of kaolinite. For the illite assemblage, is it totally residual (sedimentary diagenetic) or a part of it could be epigenetic or could have precipitated after the chlorite dissolution. Figure 7 shows that the 002/001 X-ray diffraction peak ratios in the illite assemblage indicate that trioctahedral illite is more abundant than in the other assemblages. This is logical because the dissolution of the chlorite would have enriched the fluid in Fe and Mg. The fields are not completely distinct, because there is probably a mixture of the two kinds of illite, sedimentary and epigenetic.

#### Origin of the hydrothermal fluids

The trend of decreasing temperature from 300 to 150°C with a constant salinity (Fig. 13) likely represents cooling of the fluid as it percolates up through the fractured rocks. A temperature decrease will cause silica precipitation followed by arsenopyrite when the temperature reaches 300°C. Arsenopyrite crystallization ends when the temper-

ature reaches 150°C, whereas silica will continue to precipitate at lower temperatures. The second trend with temperatures ranging from 150 to about 120°C records mixing between the cooled mineralizing fluid and another low temperature and low salinity fluid, most likely warm and exchanged meteoric water during the waning stage of the hydrothermal system.

The isotopic composition of water in equilibrium with the average SAR vein quartz  $\delta^{18}\text{O}$  value (22.9‰) is estimated at the higher temperature end member of fluid inclusion data (300°C; Fig. 13), which yields a maximum  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  value of 16.0‰ using Clayton et al. (1972; Fig. 14). Quartz veinlets in silicified and mineralized calcilutite have  $\delta^{18}\text{O}$  value similar to those from the SAR vein such that they formed from the same fluid. The oxygen isotope composition of water in equilibrium with the silicified and mineralized calcilutites (average  $\delta^{18}\text{O}$  value, 22.3‰; Table 5), calculated for the same temperature (300°C) using the calcite- $\text{H}_2\text{O}$  fractionation of O'Neil et al. (1969), yields  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  value of 16.7‰ (Fig. 14). The homoge-

neous oxygen isotope composition of SAR and veinlet quartz does not record the temperature gradient found in fluid inclusions (Fig. 13) suggesting that the bulk of the quartz most likely precipitated early, at the higher temperature end member. The similar  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  value for vein quartz and for the fluid in equilibrium with altered calcitute also suggests that the fluid composition was buffered by exchange with the carbonate wallrock at high temperature.

The oxygen isotope composition of water in equilibrium with late calcite veinlets was calculated at 4.5 and 9.0‰ respectively at 150 and 100°C using O'Neil et al. (1969). The C isotope composition of  $\text{CO}_2$  in equilibrium with calcite from the veinlets, calculated using the calcite- $\text{CO}_2$  fractionation of O'Neil et al. (1969), ranges from -0.9 to 2.1‰. These values are compatible with extensive exchange of the fluids by the host rocks.

The C and O isotopic composition of calcitutes was not modified by exchange with the hydrothermal fluids that caused silicification. Exchange with magmatic fluids is expected to cause a strong decrease in  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  of the country rocks with a positive correlation in the host rocks (Valley 1986). Thus, the C and O isotopic composition of the mineralized calcitutes provides no evidence for infiltration of a pristine magmatic fluid, consistent with the high  $\delta^{18}\text{O}$  fluid values (~16‰) calculated from hydrothermal quartz.

The most likely hypothesis is that the high  $\delta^{18}\text{O}$  fluid (~16‰) had a temperature above 300°C and a salinity of about 7 wt. % NaCl. The oxygen isotopic composition, temperature, and salinity of this fluid suggest a water/rock exchange at high temperature, but lack of hydrous vein minerals prevent us from ascertaining more closely the origin of water between metamorphic and strongly exchanged sea or meteoric water. Cooling of the high-temperature fluid lead to quartz precipitation and sulfidation of host rocks that caused precipitation of gold in arsenian pyrite rims. In the waning stages of the hydrothermal system, lower temperature and lower salinity fluids, most likely exchanged sea or meteoric water, infiltrated and mixed with the cooled down high-temperature and high-salinity early fluid to precipitate stibnite in the SAR vein (Fig. 13).

The isotopic signature of the late calcite veinlets is consistent with dilution of the high-temperature and high-salinity hydrothermal fluid by sea or meteoric water. The host rocks contain a low abundance of organic matter (Héroux and Chagnon 1986) and thus oxidation of organic matter ( $\text{CH}_4$ ) to  $\text{CO}_2$  did not change the C isotopic signature of the paragenetically late calcite veinlets. The lower  $\delta^{13}\text{C}$  values could be derived from surface water, which would be consistent with the retrograde solubility of carbonates and late paragenesis.

Timing of mineralization–alteration processes, igneous activity, and faulting

Spatial relationship of the Grand Pabos and Restigouche faults with the polymetallic base metal skarns, as well as with dike swarms (Fig. 1), suggests a genetic link between the faults, mineralization, and igneous activity. At the Reboul prospect (Fig. 1), a detailed study of crosscutting relationships between structural elements (folds, cleavages, veins, shear fractures), the three types of mineralization locally present (early Cu-Zn-Ag stratabound skarn, Cu-Zn-Pb-Ag-[Au] and Ag-Cu-Zn-Pb-[Au-Sb] northeast- and northwest-trending veins, and late Ag-Au-Zn-Pb breccia veins), and the alteration indicates that the mineralization–alteration processes occurred during the development of the Grand Pabos fault (Malo et al. 2000). Fluid inclusion data from the early Cu-Zn-Ag mineralization at Reboul, as well as from the Cu skarn at the Mid-Patapédia prospect (Fig. 1; mineral occurrence 9), indicate that a high-temperature (Reboul, 450–460°C) and high-salinity (Reboul, 35–37 wt. % eq. NaCl) magmatic fluid was involved in the genesis of both skarns (Williams-Jones 1982; Williams-Jones and Ferreira 1989; Malo et al. 2000). The zoned halos of argillaceous alteration centered on Cu skarns (Fig. 6) also support a genetic link with igneous rocks at depth. At the Reboul prospect, the two later types of mineralization and alteration facies were accompanied by a decrease in temperatures, as indicated by fluid inclusions (350–200°C), and an enrichment in precious metal (Au and Ag; Malo et al. 2000). Hydrothermal fluids were also less saline (1–9 wt. % eq. NaCl; Malo et al. 2000). At SAR-Au, the high-temperature and high-salinity magmatic fluid associated with the early development of skarns is not recognized, but hydrothermal fluids have characteristics very close to those of the two late mineralizations at the Reboul prospect (low temperature/low salinity). Limestones of the White Head Formation were already folded and cleaved at the time of alteration and emplacement of mineralized veins at the Reboul prospect, but also at SAR-Au (Fig. 3). At SAR-Au, as well as at the Reboul prospect, halos of argillic alteration are cut by the Restigouche and Grand Pabos faults, respectively, suggesting that regional alteration predate Acadian strike-slip faulting (Malo et al. 2000). However, at the Mid-Patapédia prospect (Fig. 1), hydrothermal alteration halos are found on both sides of the Restigouche fault (Duba and Williams-Jones 1983) indicating that hydrothermal fluids continued to percolate along the fault after the main Acadian dextral strike-slip motion. The Acadian faults were reactivated after the Carboniferous because the Grand Pabos fault offsets rocks of the Carboniferous basin north of Chandler (Fig. 1; see also Jutras et al. 2003), and younger fluid circulation associated with post-Acadian motion along the fault is not ruled out.

**Table 6** Comparison of the main characteristics of orogenic epizonal Au–Sb deposits, distal-disseminated Au deposits and Carlin-type Au deposits

|                                                       | Orogenic epizonal Au–Sb                                                                                                                                                                                                                                                      | Distal-disseminated Au deposits                                                                                                                                                                                            | Carlin-type Au deposits                                                                                                                                                                |
|-------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Tectonic setting                                      | Continental margin; compressional to transpressional regime; veins typically in metamorphic rocks on seaward side of continental arc <sup>c</sup><br>Epizonal Au–Sb deposits are often hosted in accretionary prism, accreted arc, turbidites and metagreywacke <sup>a</sup> | Within magmatic arc±extension <sup>f</sup>                                                                                                                                                                                 | Back-arc extension and thinning of continental crust <sup>c</sup> in diffuse magmatic arc, onset of extension <sup>f</sup>                                                             |
| Structural style                                      | Ductile to brittle-ductile, reverse, strike-slip faults or oblique-slip; anticlinal domes <sup>g</sup>                                                                                                                                                                       |                                                                                                                                                                                                                            | Long-lived, crustal fracture zones <sup>f</sup>                                                                                                                                        |
| Associated igneous rocks                              | Commonly felsic to lamprophyre dikes or continental margin batholiths <sup>d</sup>                                                                                                                                                                                           | Calc-alkaline, subduction related <sup>f</sup>                                                                                                                                                                             | Broad spatial correlation with calc-alkaline subduction-related magmatism <sup>f</sup>                                                                                                 |
| Nature and form of ore bodies                         | Veins, breccias, disseminated style <sup>g</sup>                                                                                                                                                                                                                             | Discordant and strata bound <sup>f</sup>                                                                                                                                                                                   | Discordant and strata bound <sup>f</sup>                                                                                                                                               |
| Host rocks                                            | Mafic and ultramafic volcanic rocks, intrusive rocks, BIF-chert, graywacke <sup>g</sup>                                                                                                                                                                                      | Calcareous sedimentary rocks of diverse facies and igneous intrusions <sup>f</sup>                                                                                                                                         | Calcareous sedimentary rocks of diverse facies±igneous rocks <sup>f</sup>                                                                                                              |
| Ore minerals, residence of gold and metallic minerals | Native gold, pyrite±arsenopyrite, stibnite, electrum, scheelite, galena, chalcopyrite, pyrrhotite, sphalerite <sup>a</sup>                                                                                                                                                   | Chalcopyrite, tetrahedrite, sphalerite, galena, pyrite, pyrrhotite, arsenopyrite <sup>f</sup><br><br>Au: free, inclusions in solid solutions in chalcopyrite, tetrahedrite, pyrite and arsenopyrite                        | Ionic substitution and submicron-sized grains in arsenian-pyrite <sup>h</sup> forming overgrowths on pre-ore As-free or poor and Au-free pyrite                                        |
| Metal association                                     | Au, Ag, ±As, Sb, Te, W, Bi <sup>g</sup>                                                                                                                                                                                                                                      | Various base metals, Mn, As, Sb, Te, Ag, Au±Ba <sup>f</sup>                                                                                                                                                                | Au, As, Sb, Tl, Hg±W, Te, Se, Ba <sup>f</sup>                                                                                                                                          |
| Temperature of formation                              | 150–300°C <sup>c</sup>                                                                                                                                                                                                                                                       | 200–400°C <sup>f</sup>                                                                                                                                                                                                     | 200–300°C <sup>c</sup> , 150–250°C <sup>f</sup>                                                                                                                                        |
| Depth of formation                                    | 0–6 km <sup>c</sup>                                                                                                                                                                                                                                                          | Variable, 0.5 to 8 km <sup>f</sup>                                                                                                                                                                                         | 2–3 km <sup>c</sup> ; intermediate, mainly >2 km <sup>f</sup>                                                                                                                          |
| Ore fluid composition                                 | Low salinity, aqueous-carbonic±H <sub>2</sub> S <sup>g</sup> ; 3–10 eq. wt.% NaCl; =5 mol.% CO <sub>2</sub> ; traces of CH <sub>4</sub> and N <sub>2</sub> <sup>c</sup>                                                                                                      | Variable salinity, variable CO <sub>2</sub> and H <sub>2</sub> S, ± boiling <sup>f</sup>                                                                                                                                   | ≤7 eq. wt% NaCl <sup>c</sup> low salinity, 2–4 mole % CO <sub>2</sub> , 0.01 mole % H <sub>2</sub> S <sup>f</sup>                                                                      |
| Au/Ag                                                 | 1–10 <sup>1</sup> , avg ~5 <sup>g</sup>                                                                                                                                                                                                                                      | Low, variable, up to 3 <sup>f</sup>                                                                                                                                                                                        | 0.1–10 <sup>c</sup> , high, >3 to 20 <sup>f</sup>                                                                                                                                      |
| Alteration types                                      | Carbonation, sericitization, sulfidation; skarn-like assemblages in higher temperature deposits <sup>c</sup><br>Muscovite, Ca-Fe-Mg carbonates, chlorite, albite, pyrite, tourmaline <sup>g</sup>                                                                            | Potassic, phyllic, argillic, decarbonation, silic <sup>f</sup>                                                                                                                                                             | Intense silicification; some kaolinization <sup>cf</sup>                                                                                                                               |
| Heat sources                                          | Asthenosphere, crust <sup>g</sup> ; asthenosphere upwelling to midcrustal granitoids                                                                                                                                                                                         |                                                                                                                                                                                                                            | Decarbonation, argillic alteration, silicification, sulfidation<br>In Nevada, deep crustal melting and prograde metamorphism promoted by the removal of the Farallon slab <sup>b</sup> |
| Fluid sources                                         | H <sub>2</sub> O: meteoric and/or metamorphic as a fluid source                                                                                                                                                                                                              | H <sub>2</sub> O: magmatic and meteoric <sup>f</sup> ; CO <sub>2</sub> : magmatic, decarbonation of limestone <sup>f</sup> , H <sub>2</sub> S: magmatic, sedimentary rocks <sup>f</sup> , porphyry intrusions <sup>c</sup> | H <sub>2</sub> O: meteoric and/or metamorphic; CO <sub>2</sub> : metamorphic-carbonate rocks; H <sub>2</sub> S: sedimentary-metasedimentary rocks <sup>f</sup>                         |

<sup>a</sup> Ashley and Craw (2004) and references therein; <sup>b</sup> Cline (2005); <sup>c</sup> Groves et al. (1998); <sup>d</sup> Groves et al. (2003); <sup>e</sup> Hofstra (1997); <sup>f</sup> Hofstra and Cline (2000); <sup>g</sup> Kerrich et al. (2000); <sup>h</sup> Muntean et al. (2004); <sup>i</sup> Schroeter and Poulsen (1996); <sup>j</sup> Theodore (1998)

## Comparison with Carlin-type and other types of gold deposits

Table 6 synthesizes the characteristics of three types of gold deposits: (1) orogenic epizonal Au–Sb veins, (2) distal-disseminated Au-deposits, and (3) Carlin-type gold deposits. The association with strike-slip fault and the metallic signature of the SAR-Au showing (Au–As–Sb) are characteristics common to epizonal orogenic Au–Sb veins (Groves et al. 1998). However, the nature of the host rocks, of the alteration, and of the mineralization fluid (Table 6) are not typical of epizonal Au–Sb deposits. The SAR-Au showing shares strong analogies with sedimentary rock-hosted, disseminated gold deposits. These deposits have been separated into two specific types: Carlin-type and distal-disseminated Au–Ag deposits (Johnston and Ressel 2004). Although both types of deposits share many physical and geochemical characteristics, the distal-disseminated deposits are distinguished from Carlin-type deposits, based on more definitive chemical, spatial, and/or temporal links with porphyry-related deposits (Johnston and Ressel 2004). In contrast to distal-disseminated deposits, Carlin-type deposits generally form at lower temperatures, are commonly not spatially associated with metamorphic aureoles of coeval intrusive stocks, lack Ag and base metal association, and have fluid isotope compositions suggesting evolved meteoric fluids in metasedimentary rocks as sources for ore-forming components (Johnston and Ressel 2004). Although some authors clearly distinguish distal-disseminated gold deposits from Carlin-type (Cunningham et al. 2004), others wonder whether the variability in isotopic and metal signatures across the sedimentary rock-hosted Au deposit spectrum could be related to the distance from source magmas and degree of mixing and dilution of magmatic fluid by meteoric water rather than distinguishing between mutually exclusive magmatic and amagmatic contributions (Johnston and Ressel 2004; Sillitoe 2004). The chemical distinction between both types of deposits is not obvious, as Te, W, Ag, and relatively minor quantities of Zn, Pb and Cu occur in several classic Carlin-type deposits

(Hofstra and Cline 2000). However, base metals are usually downplayed or ascribe to pre-Au diagenetic or hydrothermal activity (Sillitoe 2004). On the other hand, base metals are not reported to be anomalous in certain deposits peripheral to several intrusion-centered districts (Babcock et al. 1995). Furthermore, classic Carlin-type deposits typically lack isotope evidence for magmatic input (Hofstra and Cline 2000; Hu et al. 2002), although recent results from Deep Star, Screamer, and Getchell are consistent with contributions of magmatic volatiles and/or S (Cline et al. 2003; Heitt et al. 2003; Kesler et al. 2003). The role played by magmatism in the formation of Carlin-type deposits in Nevada is still debated (Muntean et al. 2004).

Although the spatial association of the SAR-Au showing with Cu-skarn and porphyry mineralization is characteristic of distal-disseminated Au deposits, the lack of definitive evidence for a magmatic-derived hydrothermal fluid and the absence of base metals and silver enrichment at SAR-Au showing are inconsistent with this type of deposit.

The principal characteristics of Carlin-type gold deposits from Nevada are summarized by Schroeter and Poulsen (1996), Hofstra (1997), Poulsen (1999a, b), Groves et al. (1998), Hofstra and Cline (2000), and Cline (2005) in Table 7. Carlin-type gold deposits are described as sedimentary rock-hosted disseminated gold deposits, associated with jasperoid replacements of limestones. It is notable to mention that most of the characteristics are found at the regional scale, Gaspé Peninsula, and northern New Brunswick (Fig. 1), at the district scale, southern Gaspé (Fig. 1), and at the occurrence scale, the SAR-Au showing. The most striking features found in the SAR-Au showing that are compatible with Carlin-type deposits are: (1) the calcareous nature of the host rocks; (2) the Au–As–Sb–Hg metallic signature with absence of base metals and Ag (Hofstra and Cline 2000); (3) the association with a crustal scale fault zone; (4) the hydrothermal alteration characterized by silicification, calcite and quartz veinlets at the margin of the Au-bearing zones and the occurrence of kaolinite in large halos of argillic alteration; (5) numerous felsic dikes; (6) the occurrence of Au in As-rich pyrite

**Table 7** Principal characteristics of Carlin-type deposits from Nevada (Poulsen 1999b) and their presence or absence at SAR-Au showing

| Regional scale        |   | District scale            |   | Occurrence scale            |   |
|-----------------------|---|---------------------------|---|-----------------------------|---|
| Carbonate assemblages | ✓ | Siliciclastic carbonates  | ✓ | Microscopic gold            | ✓ |
| Facies boundary       | ✓ | Thrusts (reverse faults)  | ✓ | Silicification              | ✓ |
| Major lineaments      | ✓ | Anticlines/horsts         | ✓ | As–Sb–Au–Hg                 | ✓ |
| Allochthons           | X | Strike-slip/normal faults | ✓ | Breccias                    | ✓ |
| Unconformities        | ✓ | Intrusions/stocks         | ✓ | Steep faults                | ✓ |
| Mineral belts         | ✓ | Jasperoids                | ✓ | Impure carbonate host       | ✓ |
| Magmatic belt         | ✓ | Other gold occurrences    | ✓ | Siliciclastic/volcanic caps | ✓ |
| Core complexes        | X |                           |   | Dikes                       | ✓ |

forming overgrowths on pre-ore As-free pyrite, and in arsenopyrite; (7) hydrothermal fluids mainly derived from meteoric water exchanged with host rocks at high temperature ( $>200^{\circ}$ ). In addition, Peters et al. (1997), Emsbo et al. (2003), and Nutt and Hofstra (2003) describe breccias formed by jasperoid and limestone clasts cemented by drusy quartz  $\pm$  stibnite, similar to those observed at SAR-Au showing. These breccias are interpreted by Nutt and Hofstra (2003) to be pre- or syn-ore, because the oxygen isotope compositions of drusy quartz are similar to those of gold-bearing jasperoid. In addition, at Meikle, stibnite veins cut across breccia cavities filled by ore. The silicified limestones at SAR-Au showing are comparable with the jasperoids replacement of limestones commonly found in Carlin-type gold deposits. However, the size of the SAR-Au showing is significantly smaller than in typical Carlin-type deposits in Nevada. At the regional scale (Table 7), there are differences between tectonic setting of the Nevada region and southern Gaspé Peninsula. Carlin-type deposits in Nevada are mainly hosted by Paleozoic platform rocks overthrust by offshore volcanic and siliciclastic Paleozoic rocks. During the mid-Tertiary, the region was subsequently affected by regional extension and calc-alkaline subduction-related magmatism (Hofstra and Cline 2000). Carlin-type deposits were mainly formed during this latter time interval (Hofstra et al. 1999). Temporal and spatial links with mid-Tertiary magmatic belts suggest a genetic relationship with Carlin-type gold deposits (Hofstra and Cline 2000). In the Gaspé Peninsula, the SAR-Au showing is hosted by deep-water carbonate rocks deposited in a successor basin. This basin was affected by Late Silurian normal faulting during the Salinic disturbance (Malo 2001) and subsequently folded and faulted (high angle and strike slip) during the Devonian Acadian orogeny (Malo and Kirkwood 1995). The Acadian tectonic regime in southern Gaspé is dominated by strike-slip tectonics (Malo and Kirkwood 1995), and volcanic rocks are of within-plate affinity (Bourque et al. 2001). The tectonic setting of the Carlin-type deposits in Nevada is more complex, involving more than one major orogenic event, Paleozoic and Mesozoic compressive deformation followed by Tertiary extension (Hofstra and Cline 2000). The type of magmatic regime is also very different between subduction-related magmatism in Nevada and within-plate magmatism in the Gaspé Peninsula.

### Exploration guides

Although the SAR-Au showing is small, the analogies with Carlin-type mineralizations encourages exploration for such a deposit type in the area and elsewhere in the Appalachians as already proposed in Newfoundland by Squires (2004).

Malo et al. (1998) proposed that the southwestern Gaspé area could represent an intrusion-related hydrothermal

center with proximal Cu-skarn mineralization and distal Carlin-type Au-As-Sb  $\pm$  Hg mineralization. This magmatism likely raised temperature and could have induced convection of the mineralizing fluid at depth. The distribution of magmatic rocks in the region may serve as a guide, as magmatism was probably the source of the mineralizing fluid or at least of heat necessary to convect the ore-fluid.

The quartz-stibnite-Au mineralization at SAR-Au showing is controlled by the Grand Pabos-Restigouche fault system. Structural intersections between secondary faults/shear fractures and the main Grand Pabos-Restigouche faults are prime targets in exploration for new deposits. In addition, zoned halos of clay mineral assemblages are very useful mineral exploration tools as all Au showings, as well as Cu-skarns, in the area (Fig. 6) are within clay minerals halos. A 1-km side square sampling grid seems suitable for the exploration for such halos. However, precise drawing of the halos would necessitate a sampling grid with smaller cells (about 0.5 km side square cells).

A low cost approach to support an exploration program could be a regional stream sediment survey analyzing among others As and Au with very low detection limits.

### Conclusion

This study highlights the analogy of the geological setting of the SAR area with that of regions hosting Carlin-type mineralization. The collective geological characteristics of the SAR-Au showing indicate that it shares many characteristics with the Carlin-type gold deposits of Nevada. The most diagnostic feature is the occurrence of Au in arsenian pyrite overgrowths on early and arsenic-free pyrite. In addition, the metallic signature and the alteration style are similar to those in Carlin-type mineralizations from Nevada. The mechanisms that lead to the formation of Carlin-type gold deposits are still under debate. However, the origin of the mineralizing fluid that lead to the formation of SAR-Au showing is not in contradiction with Carlin-type gold deposits.

This study reveals new types of mineralization in the Canadian Appalachians and highlights new guides for the prospecting of other occurrences, such as clay mineral halos and structural features.

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