SCAPOLITE IN TWO CANADIAN GOLD DEPOSITS: NICKEL PLATE, BRITISH COLUMBIA AND HEMLO, ONTARIO

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ABSTRACT

Scapolite from the Nickel Plate gold-skarn deposit, British Columbia, and the Archean Hemlo gold deposit, Ontario, has been studied in detail. Chlorine–carbonate scapolite is commonly present at Nickel Plate in both the mineralized and barren exoskarn and endoskarn, although it is generally more abundant within, and adjacent to, the sulfide–gold orebodies. Less commonly, scapolite also occurs in rare, vuggy cavities developed in a limestone-boulder-bearing unit (the Copperfield breccia) and in marble beyond the outer limits of the skarn envelope. Scapolite equilibria involving coexisting garnet – plagioclase – calcite – quartz in the CASCH system yielded $X(\text{CO})$ of 0.04 ± 0.02 and temperatures of 500 ± 20°C at a pressure of 1 kbar. Fluid inclusions in scapolite from exoskarn, endoskarn and a vuggy cavity yielded similar temperatures of homogenization ($250-470°C$, and mostly between $320$ and $400°C$) and salinities (15.6 to 19 wt.% NaCl equivalent). At Nickel Plate, there is no apparent correlation between the Cl content of scapolite and the spatial proximity of the mineral to ore; instead, Cl content corresponds to EqAn content, which, in turn, relates to the anorthite component of associated plagioclase. We suggest that the Cl content of scapolite is not directly proportional to the chlorinity of the coexisting fluid, but rather is strongly controlled by crystal structure (i.e., by charge-balance constraints imposed by the scapolite framework). The occurrences of Cl-bearing scapolite at the Nickel Plate deposit also provide further support for chloride complexes in the transport and deposition of gold in skarn systems. Sulfate–carbonate scapolite (EqAn$\geq50$), coexisting plagioclase (An$<:30$) and calcite at the Hemlo deposit crystallized immediately after the peak regional metamorphism and predated gold mineralization. The sulfate content of the scapolite at Hemlo is directly controlled by coexisting mineral assemblages (i.e., anhydrite-bearing and anhydrite-absent) and is consistent with the experimental calibration of Kotel'nikov (1987).

Keywords: scapolite, Cl content, crystal-structure control, fluid salinity, Nickel Plate gold-skarn deposit, British Columbia, Hemlo gold deposit, Ontario.

Nous avons étudié la scapolite du gisement aurifère de type “skarn” de Nickel Plate, en Colombie-Britannique, et du gisement aurifère de Hemlo, en Ontario. Une scapolite riche en chlore et carbonate est répandue à Nickel Plate, soit dans la zone minéralisée, soit dans l’exoskarn et l’endoskarn stériles, mais elle l’est davantage au sein des zones minéralisées en sulfures et en or, et près de celles-ci. Moins répandues sont les cavités à scapolite dans la brèche dite de Copperfield, une unité à blocs de calcaire, et dans le marbre au-delà de l’enveloppe skarnifiée. Un calcul de l’équilibre impliquant scapolite – grenat – plagioclase – calcite – quartz dans le système CASCH mène à une valeur de $X(\text{CO})$ de 0.04 ± 0.02 et une température de 500 ± 20°C pour une pression de 1 kilobar. Une étude des inclusions fluides dans la scapolite de l’exoskarn, de l’endoskarn et d’une cavité indique une variation restreinte de la température d’homogénéisation (250–470°C, et surtout entre 320 et 400°C) et une salinité de 15.6 à 19% de NaCl (ou équivalent). A Nickel Plate, il ne semble pas y avoir de corrélation entre la teneur en Cl de la scapolite et la proximité de l’échantillon au minéral. Le teneur en Cl dépendrait plutôt de la teneur équivalente en An (EqAn), qui dépend à son tour de la teneur en An du plagioclase associé. La teneur de la scapolite en Cl ne serait pas directement proportionnelle à la chlorinité de la phase fluide correspondante, mais dépendrait plutôt de contrôles cristallochimiques, et plus particulièrement des contraintes dues à la balance des charges imposées par la trame de la scapolite. La présence de la scapolite riche en chlore à Nickel Plate serait une indication de plus que des complexes à base de chlore auraient été responsables de la mobilisation et la déposition de l’or dans ces skarns. A Hemlo, la présence de scapolite à sulfate et carbonate (EqAn$\geq50$), en coexistence avec plagioclase (An$<:30$) et calcite, indique que la déposition de l’or a eu lieu tôt après les conditions maximales de métamorphisme régional, et donc avant la minéralisation. La teneur en sulfate dans ce cas dépend directement de l’assemblage de minéraux coexistants (c’est-à-dire, de la présence ou l’absence d’anhydrite), et concorde avec le calibrage expérimental de Kotel’nikov (1987).

(Mots-clés: scapolite, teneur en Cl, contrôle cristallochimique, salinité de la phase fluide, gisement or–skarn de Nickel Plate, Colombie-Britannique, gisement aurifère de Hemlo, Ontario.)
Scapolite is of petrological interest because it contains a number of important volatile species, Cl\textsuperscript{-}, CO\textsubscript{2}\textsuperscript{−}, and SO\textsubscript{4}\textsuperscript{2−} (Shaw 1960), and it has a rather wide field of stability, extending to high-T and high-P crustal conditions (Goldsmith & Newton 1977, and references therein). Several studies (e.g., Lovering & White 1964, Goldsmith & Newton 1977, Ellis 1978, Vanko & Bishop 1982, Aitken 1983, Kotel’nikov 1987) have been devoted to synthesis of various compositions of scapolite and partitioning of Cl\textsuperscript{-}, CO\textsubscript{2}\textsuperscript{−}, and SO\textsubscript{4}\textsuperscript{2−} between scapolite and coexisting fluids. More recently, scapolite equilibria based on experimental calibrations have been used to quantify physicochemical conditions of coexisting hydrothermal fluids in metamorphic terranes (e.g., Mora & Valley 1989, Moecher & Essene 1990, 1991, Oliver et al. 1992).

Scapolite is also a common gangue mineral in a wide variety of mineral deposits, particularly those of skarn type. In addition to its classic occurrences in calc-silicates (skarns) of the Grenville Province (Shaw 1960, Lentz 1991), scapolite has been documented in many other important Canadian ore deposits (e.g., Peredery et al. 1982, Thomson et al. 1985, Ray & Webster 1991, and references therein). Compared to the numerous studies of scapolite in metamorphic rocks (e.g., Mora & Valley 1989, Moecher & Essene 1990, 1991, Oliver et al. 1992) and mantle xenoliths (e.g., Lovering & White 1964), little attention has been given to scapolite in mineral deposits. Given the importance of hydrothermal fluids in the formation of ore deposits in general, and in accord with our recent efforts in documenting halogen-rich minerals in major Canadian ore deposits (Pan & Fleet 1990, 1992b, c, Pan et al. 1993, Chen et al. 1993), we decided to investigate the nature of scapolite in two well-known Canadian gold deposits: the Nickel Plate gold skarn deposit, Hedley district, British Columbia, and the Hemlo gold deposit, Ontario. The selection of the Nickel Plate deposit (217–194 Ma; Late Triassic to Early Jurassic) is particularly appropriate, because it is considered to be a classic example of a reduced gold–skarn deposit (Ettlinger et al. 1992). Moreover, scapolite is an abundant product of alteration of all the gold-bearing skarns in the Hedley district (i.e., Nickel Plate, French, Canty and Good Hope); its presence may thus be of practical significance in the exploration for new deposits of this type (Ray & Webster 1991).

Scapolite at the Archean Hemlo deposit, which is characterized by a late calc-silicate alteration, exhibits some remarkable similarities with Phanerozoic skarn deposits (Pan et al. 1991, Pan & Fleet 1992a). Scapolite at the Hemlo gold deposit crystallized after the peak of regional metamorphism (Pan & Fleet 1993) and before the gold mineralization (Pan & Fleet 1992a), yet it provides important constraints on the timing of gold mineralization and serves as an excellent example in a study of the control of mineral assemblages on the sulfate component of calcic scapolite (cf. Kotel’nikov 1987). The occurrence of Cl-rich scapolite at the Nickel Plate deposit provides an excellent opportunity to examine the role of the hydrothermal fluid on the composition of scapolite and its genetic link to gold mineralization in skarn systems. Moreover, this observation also has important implications for use of Cl content of scapolite to infer the nature and distribution of metamorphic fluids in metamorphic terranes (e.g., Mora & Valley 1989, Oliver et al. 1992).

**GEOLOGICAL SETTING AND PETROGRAPHY**

**Nickel Plate gold skarn deposit, British Columbia**

The Nickel Plate deposit and the Hedley district lie approximately 240 km east of Vancouver, in southern British Columbia. It is the largest and economically most important gold–skarn deposit in Canada, having produced almost 49 tonnes of gold, which is approximately half of the gold produced from all skarns in B.C. (Ettlinger et al. 1992). Interested readers are referred to Ray et al. (1988), Ray & Webster (1991), and Ettlinger et al. (1992) for detailed descriptions of the geological features of the district and the deposit. The deposit is hosted by thinly bedded calcareous and tuffaceous siltstones and limestones of the Upper Triassic Nicola Group, an accreted oceanic-arc assemblage. These rocks are intruded by numerous sills, dikes, and small stocks of subalkaline, calc-alkaline quartz diorite, diorite, and gabbro. The sills and dikes within the Nickel Plate orebody have undergone widespread alteration and replacement by pyroxene–garnet endoskarn, but primary igneous textures, such as a relict porphyritic texture, are commonly preserved in the endoskarn (Ettlinger et al. 1992). The exoskarn envelope, which is up to 300 m thick and outcrops over a 4-km\textsuperscript{2} area, is zoned away from intrusive contacts on both a local and deposit scale. It overprints a thick sequence of siltstone and lesser limestone (Hedley Formation), and locally extends up into an overlying limestone-boulder-bearing unit, the Copperfield breccia. Mostly, the gold–sulfide orebodies are developed close to the base of the skarn, and the central and upper portions of the envelope tend to be barren (Billingsley & Hume 1941).

Scapolite in the Nickel Plate deposit was reported by Ettlinger et al. (1992) to be present “in varying quantities throughout the deposit as an alteration product of plagioclase phenocrysts in the sills, with gold sulfide mineralization in ore zone exoskarn, and as subhedral polikloblastic crystals in marble beyond...
the outer limits of skarn formation". The scapolite is most abundant (locally making up to 10 to 20 vol.% of individual specimens) in the ore-zone exoskarn, and commonly occurs as discrete grains in veins or interstitial to garnet and clinopyroxene. In less altered samples, scapolite has also been found as a replacement after pre-existing plagioclase. Scapolite is generally rare in the endoskarn and has been observed both as replacement after plagioclase phenocrysts and in apparent equilibrium with the newly crystallized plagioclase. Coarse-grained scapolite, up to 1 cm in length, is also seen in a vuggy cavity that was found in the skarn-altered Copperfield breccia (Ray et al. 1986), where it occurs in association with diopside, plagioclase, tremolite, clinozoisite, quartz, K-feldspar, titanite, and pyrite.

Most of the scapolite samples were collected from three drillholes, all of which were drilled in different parts of the skarn envelope and intersected altered Hedley Formation rocks and minor endoskarns. Hole 261 intersected some gold–sulfide orebodies, Hole 73 cut only minor mineralization, whereas Hole 401 lay more distally from the ore zones and intersected completely barren skarn. The scapolite from the vuggy cavity was collected from the skarn-altered Copperfield breccia approximately 300 m east of the Nickel Plate deposit.

**Hemlo gold deposit, Ontario**

The Hemlo gold deposit is located 35 km east of Marathon, northwestern Ontario. It contains approximately 80 million tonnes of ore averaging 7.7 g/t Au, and hosts the three largest gold mines currently in production in Canada, namely, the Williams, Golden Giant and David Bell mines (Pan & Fleet 1992a). The general geological features of the Hemlo gold deposit and its host Archean Hemlo – Heron Bay greenstone belt have been given in Walford et al. (1986), Kuhns (1988), Corfu & Muir (1989) and Pan & Fleet (1992a, 1993). Only aspects relating to the metamorphic and hydrothermal alteration history (Pan & Fleet 1992a, 1993; Pan et al. 1991) and the scapolite-bearing rocks are given below.

All supracrustal rocks of the Hemlo – Heron Bay greenstone belt have been subjected to a complex history of deposition, deformation, metamorphism, magmatism and alteration (Pan & Fleet 1992a, c, 1993). Two episodes of regional metamorphism have been documented (Pan & Fleet 1993): an earlier medium P–T event (6–6.5 kbar and 500°C) and a later low P–T event (3–4 kbar and 550–600°C; Pan & Fleet 1993). Pan et al. (1991) documented a protracted development of skarn in the adjacent White River property along major planar structures in mafic and ultramafic metavolcanic rocks. It commenced after the peak of the second regional metamorphism and terminated with a late, low- to very-low-grade calc-silicate alteration. In all three mines of the Hemlo deposit, hydrothermal alteration has been documented in ore zones and country rocks, and includes extensive K-metasomatism (mica schists and microcline-rich rocks), sulfidation, and calc-silicate alteration, and, to a lesser extent, carbonatization, silicification and tourmalinization (Walford et al. 1986, Pan & Fleet 1992a, c). Although earlier studies (e.g., Kuhns 1988) suggested that gold mineralization of the Hemlo deposit predated the peak (second) regional metamorphism, more recent studies (e.g. Pan & Fleet 1992a, c) indicate that it postdates it.

Scapolite was first reported by Walford et al. (1986) in the hanging-wall metasedimentary rocks of the Williams mine. Subsequently, it has also been identified in the lower ore-zone of the Golden Giant mine (Kuhns 1988, Pan & Fleet 1992a). In some calciferous rocks from that zone, scapolite is a major constituent and, locally, makes up 30 vol.% of the rock. It occurs as xenoblastic to idioblastic grains (0.1 to 0.5 mm in diameter) and, locally, as large porphyroblasts (up to 2 mm in diameter), with abundant wormlike inclusions of quartz exhibiting a characteristic graphic texture (cf. Shaw 1960). The scapolite-bearing samples commonly contain a weakly developed foliation, defined by preferred orientation of brownish green hornblende and biotite, that is parallel or subparallel to the penetrative foliation of the region (related to the peak of regional metamorphism; cf. Pan & Fleet 1993). Many grains of scapolite also are parallel to the weakly developed foliation. Therefore, scapolite at the Hemlo deposit is broadly part of the peak of regional metamorphism (Kuhns 1988, Pan & Fleet 1993; see below). In addition, the brownish green hornblende in scapolite-bearing samples from the Golden Giant mine is commonly partly replaced by either actinolite alone or aggregates of actinolite, prehnite, pumpellyite, titanite, allanite, chlorite, and albite, which are also locally present in cross-cutting veins: this assemblage and its mode of occurrence are typical of the late calc-silicate alteration at the Hemlo gold deposit (Pan & Fleet 1992a). However, this late calc-silicate alteration is generally not well developed within scapolite-bearing samples of the Williams mine. The scapolite-bearing calciferous rocks at the Hemlo deposit may be divided into two types: anhydrite-bearing and anhydrite-absent. All grains of anhydrite and most of the grains of calcite appear to be paragenetically early. Kuhns (1988) documented anhydrite as 0.1 to 5 cm elongate lenses or pods aligned parallel to the penetrative foliation of the region. Similar to its counterparts in other rock types of the Hemlo gold deposit (Michibayshi & Jaireth 1991), at least two generations of barite have been recognized in the scapolite-bearing samples: an earlier one associated with the brownish green hornblende and scapolite, and a later one in the calc-silicate aggregates and veins. A few grains of calcite and pyrite also
occur in the calc-silicate aggregates and veins, irrespective of whether or not anhydrite is present in the sample.

**Composition and Relationship with Plagioclase**

Chemical compositions of scapolite and the associated minerals were analyzed using the JEOL JXA-8600 Superprobe equipped with four automated wavelength-dispersion spectrometers (WDS) at the University of Western Ontario (UWO). Operating conditions included 15 kV accelerating voltage, 10 nA beam current, 2-5 μm beam diameter, and 20 second counting time. Well-characterized minerals, including tugtupite for Cl and scapolite ON-70 of Evans et al. (1969) for S, were used as standards. The scapolite and associated minerals from the vuggy cavity in the skarn-altered Copperfield breccia were analyzed using the JEOL JXA-8600 Superprobe with three WDS at the University of Saskatchewan and similar operating conditions and standards. All chemical compositions of scapolite and associated plagioclase at the Nickel Plate deposit and Hemlo deposit are illustrated in Figure 1, and representative data are given in Table 1. Chemical compositions of other skarn minerals (e.g., garnet and clinopyroxene) at the Nickel Plate deposit can be found in Ettlinger et al. (1992). A complete listing of compositions of scapolite and other minerals in two scapolite-bearing samples of the Hemlo deposit are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A 0S2.

Scapolite in the exoskarn at the Nickel Plate deposit exhibits wide ranges of variation in both EqAn [31 to 52 mol%]; where EqAn = 100(Al-3)/3 and Cl (1.7 to 2.9 wt.%; Table 1), which are correlated with each other and, in turn, correlate with the An content of coexisting plagioclase (Table 1, Fig. 1). Despite the apparent higher modal abundance of scapolite in the mineralized exoskarn relative to the unmineralized exoskarn, there is no apparent relationship between the Cl content of scapolite and the proximity of the mineral to ore. Most interestingly, scapolite that replaces pre-existing calcic plagioclase (An$_{70-80}$) in the exoskarn has been found to be the most Al-rich (EqAn 57–59) and Cl-poor (0.5 wt.%; Table 1). Compared to its counterpart in the exoskarn, scapolite in the endoskarn exhibits small ranges of variation in both EqAn (40 to 51) and Cl (1.8 to 2.6 wt.% Cl; Table 1), which are also related to the compositional

![Fig. 1. Compositions of scapolite (solid symbols) and associated plagioclase (open symbols) on a plot Cl/(Cl+CO$_3$+SO$_4$) versus EqAn (= 100(Al-3)/3). Dashed lines outline the compositional field of scapolite (cf. Evans et al. 1969). Only pairs of coexisting scapolite–plagioclase (circles) in endoskarn and exoskarn of the Nickel Plate deposit are connected by solid tie-lines; triangles and dotted tie-lines represent Nickel Plate scapolite replacing relict phenocrysts of plagioclase; diamonds, Nickel Plate scapolite from a vuggy cavity in the Copperfield breccia, and rectangles, scapolite from the Hemlo gold deposit.](image-url)
SCAPOLITE IN TWO CANADIAN GOLD DEPOSITS

TABLE 1. COMPOSITIONS OF SCAPOLITE AND ASSOCIATED PLAGIOCLASE

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<th>Locality</th>
<th>Nickel Plate</th>
<th>Hemlo</th>
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<td>Sample</td>
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<td>261-13</td>
</tr>
<tr>
<td>SiO₂</td>
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<td>50.75</td>
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<td>TiO₂</td>
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<td>CO₃⁺</td>
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</tr>
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<td>O=F,Cl</td>
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<td>Total</td>
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<td>100.55</td>
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Chemical formulae calculated on the basis of 16 cations

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<th>Hemlo</th>
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<tr>
<td>Al</td>
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<td>4.533</td>
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<tr>
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<tr>
<td>Mg</td>
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<td>0.000</td>
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<tr>
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<td>K</td>
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<tr>
<td>EqAn</td>
<td>45.4</td>
<td>51.1</td>
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Sample 401-12 is an endoskarn; 261-13, 73-1-8 and 73-1-5, essoskarns; HD55, cavity in Copperfield breccia; GG1, anhydrite-bearing; GG2, anhydrite-absent. *: total iron content as FeO; †: calculated from stoichiometry; EqAn, equivalent anorthite component = 100x(Al-3)/3; **: relict plagioclase; ‡: K₋₁₋₂₋₃₋₄₋₅₋₆₋₇₋₈₋₉₋₁₀₋₁₁₋₁₂₋₁₃₋₁₄₋₁₅₋₁₆₋₁₇₋₁₈₋₁₉₋₂₀₋₂₁₋₂²₋₂₃₋₂₄₋₂₅₋₂₆₋₂₇₋₂₈₋₂₉₋₃₀₋₃₁. The samples 401-12 is an endoskarn: 261-13, 73-1-8 and 73-1-5, essoskarns; HD55, cavity in Copperfield breccia; GG1, anhydrite-bearing; GG2, anhydrite-absent. *: total iron content as FeO; †: calculated from stoichiometry; EqAn, equivalent anorthite component = 100x(Al-3)/3; **: relict plagioclase; ‡: K₋₁₋₂₋₃₋₄₋₅₋₆₋₇₋₈₋₉₋₁₀₋₁₁₋₁₂₋₁₃₋₁₄₋₁₅₋₁₆₋₁₇₋₁₈₋₁₉₋₂₀₋₂₁₋₂²₋₂₃₋₂₄₋₂₅₋₂₆₋₂₇₋₂₈₋₂₉₋₃₀₋₃₁.

difference in associated plagioclase (Table 1, Fig. 1). Grains of scapolite from the vuggy cavity in the Copperfield breccia, although homogeneous within individual grains, vary in EqAn and Cl from 38 mol% and 2.1 wt.% to 48 mol% and 1.4 wt.% respectively, and, again, correspond closely to the An content of the associated sodic plagioclase (Table 1). More calcic plagioclase (An<30) also occurs in this cavity sample, but has not been found to be in direct contact with scapolite.

At the Hemlo gold deposit, scapolite specimens from the Golden Giant mine and the Williams mine are compositionally indistinguishable. They contain no significant Cl content (typically with less than 0.05 wt.% Cl), but have a high content of sulfate (Table 1). The scapolite in all eight anhydrite-bearing samples is remarkably constant in its sulfate content at 1.9 ± 0.1 wt.% SO₄. The scapolite in six anhydrite-absent samples, however, exhibits a wide range of variation in sulfate content, from 0.5 to 1.4 wt.% SO₄. The plagioclase coexisting with scapolite at the Hemlo deposit ranges from An<30 to An<35.

STUDY OF FLUID INCLUSIONS

Fluid inclusions in skarn minerals (garnet, clinopyroxene, quartz and scapolite) of the Nickel Plate deposit have been investigated previously by Ettlinger et al. (1992). These authors obtained large variations in homogenization temperatures of fluid inclusions in garnet (210–730°C; average 384°C), clinopyroxene (250–695°C; average 386°C) and quartz (320–540°C; average 408°C) and observed systematic decreases in these homogenization temperatures away
from the diorite dikes. Ettlinger et al. also observed that the fluid inclusions in scapolite at the Nickel Plate deposit have much lower temperatures of homogenization (320–400°C; average 348°C) than those in garnet, clinopyroxene and quartz. Salinity of the fluid was estimated from fluid inclusions in garnet and clinopyroxene to be 18.3 and 9.7 wt.% NaCl equivalent, respectively. In addition, Ettlinger et al. observed the presence, although rare, of halite daughter crystals in clinopyroxene and quartz and, for these fluids, obtained a total fluid salinity of 32.7 wt.% NaCl equivalent in the former and 37.9 wt.% in the latter.

In the present study, we investigated fluid inclusions in scapolite from three types of occurrences at Nickel Plate, namely from endoskarn, from exoskarn (largely representing the Hedley Formation siltstone) and from the vuggy cavity in the Copperfield breccia. Microthermometric data on fluid inclusions in this study were obtained using a Linkam TH600 programmable cooling–heating stage at UWO, operated according to the guidelines of Macdonald & Spooner (1981). Homogenization temperatures of fluid inclusions in scapolite from all three occurrences are similar and generally within the range of 320° to 400°C (Fig. 2a), as previously established by Ettlinger et al. (1992). However, a few outliers (e.g., 250°C and 470°C) also have been measured (Fig. 2a). Surprisingly, no halite daughter crystals (cf. Ettlinger et al. 1992) were found in any fluid inclusions in scapolite examined in this study. No evidence was found for a CO₂-rich liquid or the presence of CO₂ hydrate during freezing experiments. Most fluid inclusions in scapolite were found not to be suitable for estimation of salinity by measurement of the final ice-melting temperatures, owing to either extremely small size (<5 μm in diameter) or lack of freezing (down to −150°C; see also Ettlinger et al. 1992, Mora & Valley 1989). A few fluid inclusions that were suitable for measurement yielded similar values of the final ice-melting temperature, in the range of −15.4°C to −11.6°C for scapolite from three types of occurrences (Fig. 2b), corresponding to a fluid salinity of 15.6 to 19.0 wt.% NaCl equivalent (Bodnar 1993). This is within the range of the findings of Ettlinger et al. (1992), estimated from fluid inclusions in garnet, clinopyroxene and quartz grains (see above).

Pan & Fleet (1992a) have investigated fluid inclusions in quartz and calcite associated with late calc-silicate veins in the Hemlo deposit. However, a comprehensive study of fluid inclusions in minerals representative of all paragenetic sequences, particularly those corresponding to the two episodes of regional metamorphism (Pan & Fleet 1993) is still lacking. In the present study, we did make an attempt to investigate fluid inclusions in scapolite from the Hemlo deposit. Unfortunately, fluid inclusions are extremely rare (more than 30 grains examined), and none suitable for microthermometric measurements was found.

**DISCUSSION**

The scapolite samples in the two Canadian gold deposits are clearly distinct with respect to their chemical compositions: the sodic chlorine–carbonate variety is present at the Nickel Plate deposit, and the calcic sulfate–carbonate variety is present at the Hemlo gold deposit. They, in turn, reflect marked differences in physiochemical conditions at the time of their formation in these two deposits.

**Sodic chlorine–carbonate scapolite**

The replacement of scapolite after relict phenocrysts of plagioclase in several samples of the Nickel Plate deposit is a clear indication of disequilibrium. However, scapolite and associated garnet, plagioclase, and calcite in other samples do exhibit mutual contacts and have systematic variations in chemical composi-
tions (e.g., Fig. 1), suggesting that equilibrium (at least on a local scale) most likely was attained. Therefore, scapolite equilibria of coexisting scapolite – garnet – plagioclase – calcite – quartz in the latter samples may be used to calculate $X(\text{CO}_2)$ (Moecher & Essene 1990, 1991) during the skarn formation at Nickel Plate. The scapolite equilibria computed with the GEO-CALC programs of Brown et al. (1988) using the internally consistent thermodynamic data-set of Berman (1988), analytical compositions of scapolite (ideal activity model), garnet (rim composition; activity model of Berman 1990), plagioclase (activity model of Furfman & Lindsley 1988) and calcite, and the equation of state of Kerrick & Jacobs (1981), yielded $X(\text{CO}_2)$ values at 0.04 ± 0.02 and temperatures at 500 ± 20°C at 1 kbar (Fig. 3). Scapolite equilibria based on the method of Moecher & Essene (1990, 1991) gave similar $X(\text{CO}_2)$ values, in the range 0.03–0.08 at a temperature of 500°C and a pressure of 1 kbar. The value of 1 kbar was taken from Ettlinger et al. (1992), who estimated it based on several geological constraints and considered it to be a close approximation of the pressure during skarn formation at Nickel Plate. It is noteworthy that the homogenization temperatures of fluid inclusions in scapolite, after a correction of about 100°C for a pressure of 1 kbar (Potter 1977), are in excellent agreement with the calculated temperatures from scapolite equilibria. Moreover, a reduction in pressure used in the calculation of scapolite equilibria would only slightly increase the calculated $X(\text{CO}_2)$ value (e.g., 0.1 ± 0.02 at 0.5 kbar), but not the temperature.

Fig. 3. Calculated phase-diagram of the system CaO-Al₂O₃-SiO₂-CO₂-H₂O (CASCH) for the scapolite – plagioclase – garnet – calcite – quartz assemblage of the Nickel Plate deposit. Dashed lines represent metastable extensions; An, anorthite; αQz, α-quartz; Cc, calcite; Gr, grossular; Me, meionite.
The experimental results of Ellis (1978) have been used by Mora & Valley (1989) and Oliver et al. (1992) to estimate the salinity of metamorphic fluids based on the composition of Cl-bearing scapolite. Ellis (1978) considered the equilibrium between scapolite and fluid, for scapolite of fixed EqAn content, from exchange of the salt components:

\[
\frac{\text{NaCl}_{(\text{scapolite})} + \text{CaCO}_3_{(\text{fluid})}}{\text{CaCO}_3_{(\text{scapolite})} + \text{NaCl}_{(\text{fluid})}} \rightleftharpoons \text{(1)}
\]

and fitted his experimental data of 750°C and 4 kbar to an expression \(\ln K_D = -0.0028(X_{\text{Al}})_{\text{eq}}^{5.5580}\), where \(K_D = (X_{\text{Me}}/X_{\text{Ma}})(X_{\text{NaCl}})/X_{\text{CaCO}_3}\), \(X_{\text{Al}}\) is the atomic Al/(Al + Si) ratio in scapolite, and Me and Ma stand for the calcic and sodic end-members, meionite and marialite, respectively. He suggested that if the mixing is ideal, the activity of NaCl in fluids coexisting with scapolite grown at temperature and pressure other than those of the experiments can be calculated from this equation for \(K_D\). In applying this expression to their natural Cl-rich scapolite, Mora & Valley (1989) recognized a number of potential problems: e.g., too high a temperature in the experiments of Ellis (1978) and uncertainty regarding the NaCl – H₂O – CO₂ fluid [including fluid immiscibility; e.g., Johnson (1991)]. We believe that reaction (1) itself is inadequate, as it has long been known that two substitutions, NaCl ⇌ CaCO₃ and Na + Si ⇌ Ca + Al, acting together are responsible for the compositional variation in scapolite from Me₄ to Me₇₅ (Evans et al. 1969). More recent work has established that they do not operate independently (Chamberlain et al. 1985, Hassan & Buseck 1988). Therefore, the reaction involving marialite and meionite must be written as:

\[
\begin{align*}
3 \text{anorthite} + \text{marialite} + \text{CaCO}_3 &= 3 \text{albite} + \text{meionite} + \text{NaCl} \\
(\text{Orville 1975})
\end{align*}
\]  

(2)

and the mole fraction of marialite in scapolite is not feasible. Also, plagioclase coexisting with scapolite commonly varies widely and systematically in composition (Shaw 1960, Mora & Valley 1989). Indeed, the An content of plagioclase in Ellis (1978, his Table 4) also varies systematically with the EqAn content of coexisting scapolite.

If we consider constant T, P and \((a_{\text{NaCl}}/a_{\text{CaCO}_3})\) ratio, the equilibrium constant for reaction (2) becomes

\[
K_{T,P,NaCl/\text{CaCO}_3} = (a_{\text{Al}}/a_{\text{Ar}})^3(a_{\text{Me}}/a_{\text{Ma}}),
\]

and the mole fraction of marialite in scapolite is directly related to the composition of coexisting plagioclase, ideal mixing being assumed. The commonness of a strong correlation between the compositions of scapolite and coexisting plagioclase in nature (Shaw 1960, Mora & Valley 1989; Fig. 1) indicates that \(a_{\text{NaCl}}/a_{\text{CaCO}_3}\) in the fluid does not have a direct control on the composition of scapolite. Indeed, the calculated values of \(K_{T,P,NaCl/\text{CaCO}_3}\) for coexisting scapolite and plagioclase in both exoskarn and endoskarn of the Nickel Plate deposit are remarkably similar at 50 ± 5 (Table 1). The similarities in homogenization temperature and estimated salinity of all suitable fluid inclusions in scapolite from the Nickel Plate deposit (Fig. 2) seem to indicate similar physicochemical conditions among all three types of occurrences at the time of crystallization, although it is possible also that they are related to a particular population of fluid inclusions measured. It is noteworthy that Ettlinger et al. (1992) have documented systematic decreases in homogenization temperature of fluid inclusions in garnet and clinopyroxene away from the diorite sills and dikes at the Nickel Plate deposit.

Undoubtedly, the presence of Cl-rich scapolite in mineral deposits is indicative of Cl in the fluid (Orville 1975, Ellis 1978, Mora & Valley 1989), especially where scapolite is modally abundant. However, the Cl content in scapolite is not directly proportional to the chorinility of the coexisting fluid (e.g., Ellis 1978). A quantitative calculation of fluid salinity based on scapolite must await experimental calibration of reaction (2) at lower temperatures (e.g., 400–600°C, work in progress; cf. Vank & Bishop 1982, Mora and Valley 1989). It is noteworthy that several studies (e.g., Mora & Valley 1989, Oliver et al. 1992) have attributed the wide range of Cl variations in scapolite from metamorphic terranes to fluid heterogeneity. Oliver et al. (1992) did establish heterogeneity of metamorphic fluids from estimates of reaction progress and other mineral equilibria, yet their \(a_{\text{NaCl}}/a_{\text{H}_2\text{O}}\) values inferred from scapolite compositions exhibit the widest variation. The Cl content in biotite coexisting with scapolite studied by Mora & Valley (1989) is clustered and appears to correlate negatively with the \(X(\text{Mg})\) content in biotite (their Fig. 5), pointing to a crystal-structure control (cf. Volfinger et al.
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1985). As a result, the calculated log(\(f_{HF}/f_{HCl}\)) ratios based on biotite in Mora & Valley (1989, their Fig. 6) are essentially constant within a given metamorphic zone, except for the biotite zone, in which two distinct (but not scattered) groups exist, and vary systematically with metamorphic grade. The present study suggests that the compositional variations in scapolite in metamorphic terranes could be partly related to its equilibrium relationship with coexisting plagioclase. Therefore, a compositional variation of scapolite alone cannot be taken as evidence for fluid heterogeneity in metamorphic terranes. Similarly, Moecher & Essene (1990, 1991) recognized that the CO\(_2\) content of scapolite was not directly proportional to the X(CO\(_2\)) values in metamorphic fluids, but was controlled by a(CO\(_2\)) of the mineral assemblage as a whole.

**Crystal-structure control on the Cl content in scapolite**

A crystal-structure control on the Cl content in hydroxyl-bearing minerals has been emphasized by a number of investigators (e.g., for mica and amphibole by Volfinger et al. 1985, Enami et al. 1992, Oberti et al. 1993). In a study of Cl-bearing amphibole in the Salton Sea geothermal system, for example, Enami et al. (1992) established that the Cl content of an amphibole increases with increasing chlorinity of the coexisting fluid only at low chlorinity of the fluid, whereas crystal-structure controls of the amphibole itself (Oberti et al. 1993) are more important in highly saline fluids. Crystal-structure controls on the Cl content in amphiboles are indicated by positive correlations with Fe\(^{2+}\), VAl and K (Enami et al. 1992, Pan & Fleet 1992b, Oberti et al. 1993, and references therein). Similarly, the negative correlation between Cl and EqAn in scapolite (Fig. 1) is also indicative of a crystal-structure control on the incorporation of Cl into this mineral.

In scapolite, large anions, including Cl\(^-\), CO\(_3\)^{2-} and SO\(_4\)^{2-}, are accommodated in cages or channels within a framework of AlO\(_4\) and SiO\(_4\) tetrahedra. Lin (1975) suggested that tilting of the CO\(_3\)^{2-} group causes displacement of Ca\(^{2+}\) and Na\(^+\) cations along the c axis and ordering of Al\(^{3+}\) and Si\(^{4+}\) cations. He attributed the compositional variations to local neutralization of electrostatic charges between the tilted CO\(_3\)^{2-} groups, the displaced Ca and Na atoms, and the framework of tetrahedra. Chamberlain et al. (1985) demonstrated the local balance of charges between the Na\(^+\) and Cl\(^-\) and Ca\(^{2+}\) and CO\(_3\)^{2-} in scapolite by calculations of electrostatic energy. However, NaCl and CaCO\(_3\) do not exist as discrete molecular entities within the cage positions of the scapolite framework. In marialite, for example, as in sodalite (e.g., Fleet 1989), the Cl\(^-\) anion is coordinated to four Na\(^+\) (in a ClNa\(_4\) group), and the excess charge on each Na\(^+\) cation is compensated by bonding with adjacent atoms of bridging oxygen of the aluminosilicate framework. Thus, substitution of Cl\(^-\) by CO\(_3\)^{2-} (or SO\(_4\)^{2-}) and Na\(^+\) by Ca\(^{2+}\) in scapolite requires a compensating substitution of Si\(^{4+}\) by Al\(^{3+}\) in the framework, but the Al/Si ratio is buffered locally by whole-rock composition. This accounts directly for the strong correlation between the compositions of scapolite and coexisting plagioclase. Hassan & Buseck (1988) showed evidence for two compositional series within scapolite (coupled replacement of [Na\(_2\)Cl]Si\(_4\), by [NaCa\(_2\)CO\(_3\)]Al\(_2\) between 0 and 75% meionite, and [NaCa\(_2\)CO\(_3\)]Si\(_4\) by [Ca\(_4\)CO\(_3\)]Al between 75 and 100% meionite), which points to a second-order correlation with coexisting plagioclase composition, that is possibly related to metamorphic grade.

As for high-temperature plagioclase, the structure-composition relationship for scapolite requires disorder of framework cations (Al\(^{3+}\), Si\(^{4+}\)). The three nonequivalent tetrahedrally coordinated sites in the scapolite structure permit natural scapolite of EqAn 33 composition to be ideally ordered, but all other compositions of scapolite exhibit positional disorder of Al and Si (e.g., Oterdoom & Wenk 1983, Sherriff et al. 1987). However, this disorder should have little effect on the present discussion because our crystal-chemical explanation for the correlation between the compositions of coexisting scapolite and plagioclase depends on local balance of charges only.

**Calcic sulfate-carbonate scapolite**

Mora & Valley (1991) have shown that the compositions of scapolite porphyroblasts in regionally metamorphosed sedimentary rocks northwest of the Idaho batholith have been affected by fluid–rock interaction during retrograde alteration. As mentioned above, the scapolite-bearing samples of the Golden Giant mine do show extensive hydrothermal replacement of the late calc-silicate type. Pan & Fleet (1992a) have documented that the fluid responsible for the late calc-silicate alteration at the Hemlo deposit and elsewhere in the Hemlo – Heron Bay greenstone belt (Pan et al. 1991) was moderately to highly saline (up to 37 wt.% NaCl equivalent). The scapolite in the Golden Giant mine would most likely have been Cl-bearing, if an exchange with the saline fluid had occurred. However, the level of chlorine is characteristically low in scapolite of the Golden Giant mine (Table 1). Moreover, the compositions of scapolite in the altered (and mineralized) samples of the Golden Giant mine are similar to those of its counterpart in relatively unaltered samples of the Williams mine. We conclude, therefore, that the scapolite at the Hemlo deposit has not been greatly affected by subsequent hydrothermal alteration and reflects its composition at the time of crystallization.

Goldsmith & Newton (1977) demonstrated experimentally that end-member carbonate and sulfate meionites are stable only above 870°C; the stability of
the latter is favored by pressure. They also showed that Na stabilizes scapolite to lower temperatures. Oterdoom & Gunter (1983) suggested that carbonate scapolite has a lower stability-limit of about 550°C, where it has a composition of EqAn 67 and coexists with calcite and intermediate plagioclase. The compositions of coexisting hornblende and plagioclase in the scapolite-bearing samples at the Hemlo gold deposit are indicative of a temperature of 550°C and a pressure of 4 kbar (cf. Plyusnina 1982), in reasonable agreement with T-P estimates for the peak regional metamorphism from metapelitic assemblages (550–600°C and 3–4 kbar; Pan & Fleet 1993). Field occurrences and textural evidence suggest that the scapolite-bearing assemblages and other calc-silicate assemblages at the Hemlo deposit crystallized after the peak of regional metamorphism (see also Walford et al. 1986). Indeed, skarn-like calc-silicate assemblages associated with metamorphosed mafic and ultramafic volcanic rocks elsewhere in the Hemlo – Heron Bay greenstone belt, exhibiting similar textures (e.g., their weakly developed foliation also parallel or subparallel to the penetrative foliation of the region), clearly represent replacements after the metamorphic assemblages and have been suggested to have formed immediately after the peak of the regional metamorphism (Pan et al. 1991). The sulfate–carbonate scapolite (EqAn65) coexisting with calcite and plagioclase (An30-35) at the Hemlo gold deposit represents one of the lowest-grade examples of carbonate-rich scapolite reported (Oterdoom & Gunter 1983, Kassoli-Fournaraki 1991). The significant sulfate content of scapolite from the Hemlo deposit (Table 1) most likely played a role on its stability at such low temperatures through the entropy of mixing sulfate and carbonate groups (cf. Goldsmith & Newton 1977). It is unlikely, however, that the sulfate content of the scapolite is related to the metamorphic pressure (e.g., Goldsmith & Newton 1977), which was typically low during and after the peak regional metamorphism (andalusite–sillimanite series; Pan & Fleet 1993).

Kotel’nikov (1987) investigated the exchange reaction for sulfate-bearing scapolite at 600–800°C and 2 kbar in the presence of anhydrite and calcite. He found that the inferred free energy of this exchange reaction is almost independent of pressure, and obtained the following expression: ln[(CO₂/2SO₄)₂] = ln[X(Me-CO₂)/X(Me-SO₄)] + (58600 – 15T)/RT, where T is in Kelvin. We have applied this expression to the sulfate–carbonate scapolite of the Hemlo deposit. Scapolite in the anhydrite-bearing samples yielded a ln[(CO₂/2SO₄)₂] ratio of about 29.5 at 550°C (see above), consistent with the coexistence of anhydrite and calcite (Fig. 4). In contrast, the scapolite in the anhydrite-absent samples yielded ln[(CO₂/2SO₄)₂] ratios ranging from 30 to 31 at 550°C, outside of the stability field of anhydrite (Fig. 4).

### Association with gold mineralization

Accessory scapolite occurs in some Fe and reduced W skarns worldwide (Shaw 1960, Sangster 1969, Podlessky et al. 1991, Lowell 1991), as well as in some gold-bearing skarns (Ettlinger & Ray 1989, Meinert 1989, Theodore et al. 1991). However, the scapolite at Nickel Plate and all other Hedley gold–skarn deposits is distinct because of its local abundance, and its temporal and spatial association with gold mineralization (Ray & Webster 1991, Ettlinger et al. 1992). Thus, the presence of abundant scapolite in a skarn, although not easily detected in the field, could be a significant tool for the exploration of other Hedley-type gold–skarn deposits (Ray & Webster 1991, Ettlinger et al. 1992).

This study indicates that the scapolite at Nickel Plate is Cl-rich, as is the scapolite associated with the Ajax and Ingerbell – Copper Mountain Cu–Au porphyry deposits in British Columbia (Ross 1993, authors’ unpubl. data). This fact, together with the evidence for the presence of saline fluids in some gold-bearing skarns (e.g., Cl-bearing amphiboles and fluid-inclusion data; Ettlinger & Ray 1989, Theodore et al. 1991, and references therein; Ettlinger et al. 1992, and above), support the idea that chloride complexes are important in the transport and deposition of gold in skarn and porphyry systems (Meinert 1984).
Transport of gold as chloride (or sulfide–chloride) complexes under relatively saline and high-temperature conditions has been suggested for other geological environments [e.g., volcanogenic massive sulfide deposits: Large et al. (1989); late magmatic systems: Fleet & Wu (1993)].

The lack of Cl in scapolite at Hemlo does not preclude the transport and deposition of gold by chloride complexes in this deposit, because this mineral crystallized immediately after the peak of the regional metamorphism and predated gold mineralization (Pan & Fleet 1992a). In fact, the hydrothermal fluid responsible for gold mineralization at the Hemlo deposit has been shown to be moderately to highly saline (Pan & Fleet 1992a). The present observations on the scapolite-bearing samples also support our earlier suggestion (Pan & Fleet 1992a, c) that gold mineralization at the Hemlo deposit most likely occurred during the late calc-silicate alteration. The scapolite and late calc-silicates are spatially related because all mineralizing fluids at Hemlo were focused along the same ancient conduit, that formed within the dilatant Hemlo Shear Zone (Pan et al. 1991, Pan & Fleet 1992a, c).

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