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IMPACT-RELATED Ca-METASOMATISM IN CRYSTALLINE TARGET-ROCKS FROM THE CHARLEVOIX STRUCTURE, QUEBEC, CANADA

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Abstract

The mineralogy and microstructure of Ca-rich metasomatic zones developed in crystalline target-rocks from the 54-km-diameter Charlevoix impact structure, in eastern Quebec, have been investigated by optical microscopy, analytical scanning electron microscopy and cathodoluminescence microscopy. The zones occur as discrete lenses (<0.5 m long) and as veins (<0.5 m wide) associated with regions of locally enhanced fracturing within Grenville Province charnockitic gneisses. The dominant metasomatic assemblage is prehnite + quartz ± calcite. Mineral fragments of the host gneiss also occur within the Ca-rich zones. Reaction of the fluid with the host gneiss and its entrained fragments is revealed by the partial replacement of shocked quartz by aggregates of authigenic quartz. Prehnite is considered to have supplanted the anorthite component of the host plagioclase. The predominance of prehnite indicates that precipitation mainly occurred at 250–380°C, probably following a higher-temperature phase. Mineralized cavities within the Ca-rich zones are themselves cross-cut by prehnite-filled fractures, and quartz partly shows a fibrous or spherulitic structure, indicating successive stages of precipitation during cooling. The Ca-metasomatic event occurred after the impact because it affected already shocked rocks and because the metasomatic minerals show no evidence of shock. The relatively high temperature of the fluid and the restriction of the Ca-rich zones to the impact structure suggest that the metasomatism is impact-related. Thermal energy to drive the hydrothermal system would have come from a combination of overlying impact-melt sheet and fallback, central uplift elevation and waste shock-induced heat. Given the Ca- and CO_2-poor composition of the host gneiss, hydrothermal circulation through overlying carbonaceous Ordovician target-rocks may have provided an additional source for these components. Silicon, Al and Fe^{3+} were probably derived from the reaction of the fluid with the host gneiss. Ca-rich metasomatism was caused by the relatively short-lived (<1 Ma) thermal convection of aqueous fluids through shock-heated target-rocks that had acquired enhanced permeability due to impact-induced fracturing, with subsequent precipitation occurring in high-porosity zones.

Keywords: Ca metasomatism, prehnite, post-impact hydrothermal activity, planar deformation features, cathodoluminescence, shock features, Charlevoix impact structure, Quebec.

Sommaire

Nous avons étudié la minéralogie et la microstructure de zones métasomatiques enrichies en Ca développées dans les roches cristallines cibles de l'impact météoritique de la structure de Charlevoix, d'un diamètre de 54 km, dans l'est du Québec; nous nous sommes servis de la microscopie optique, microscopie électronique à balayage et cathodoluminescence. Les zones forment des lentilles distinctes de moins de 0.5 m en longueur et des veines de moins de 0.5 m de large, associées aux régions de fractures intensifiées dans le gneiss charnockitique du socle grenvillien. L'assemblage métasomatique prédominant est prehnite + quartz ± calcite. Des fragments des minéraux du gneiss hôte se trouvent au sein des zones enrichies en Ca. Une réaction avec le gneiss hôte et les fragments entraînés est mise en évidence par le remplacement partiel du quartz déformé par des aggrégats de quartz authigène. La prehnite aurait cru aux dépens de la composante anorthite du plagioclase. La prédominance de la prehnite indique une précipitation surtout dans l'intervalle 250–380°C, probablement suite à une phase de plus haute température. Les cavités minéralisées des zones riches en Ca sont elles-mêmes recoupées par des fractures remplies de prehnite, et le quartz montre en partie une texture fibreuse ou sphérulitique, indication de stades successifs de précipitation au cours du refroidissement. La métasomatose a eu lieu après l'impact: elle affecte les roches ayant subi le choc, et les minéraux néoformés n'ont pas subi ce choc. La température relativement élevée de la phase fluide et la restriction des zones riches en Ca aux roches affectées par l'impact

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montrent que la métasomatose était liée à l'impact. L'énergie thermique requise pour activer le système hydrothermal aurait été fournie par la couche de liquide silicaté et de débris formés par l'impact, la remontée centrale des roches enfouies, et l'excédent de chaleur dû à l'onde de choc. A cause de la composition pauvre en Ca et CO_2 du socle, les fluides ont possiblement traversé les séquences de calcaire Ordovicien. Les éléments Si, Al et Fe^{3+} seraient dérivés de la réaction de la phase fluide avec le gneiss du socle. La mobilisation du Ca aurait été causée par la convection relativement brève (<1 Ma) de fluides aqueux dans un amas de roches bréchifiées à cause de l'impact, et a mené à une précipitation subséquente dans des zones à porosité élevée.

(Traduit par la Rédaction)

Mots-clés: métasomatose calcique, prehnite, activité hydrothermale post-impact, plans de déformation lamellaire, cathodoluminescence, phénomènes de choc, structure d'impact de Charlevoix, Québec.

Introduction

Post-impact fluid flow can be an important process during the cooling of freshly generated impact structures. It can result in economic mineralization (Naumov 2002) and may facilitate favorable conditions for life on Earth (Osinski *et al.* 2001) and possibly other planets (Rathbun & Squyres 2002). Fluid circulation results from the development of heat and pressure gradients in permeable target-rocks. The fluid composition is influenced by the reaction of superficial, meteoric and ground waters with the target rocks, as well as by the products of impact-induced dehydration, degassing and melting (*e.g.*, Boer *et al.* 1996, McCarville & Crossey 1996, Osinski *et al.* 2001, Kirsimäe *et al.* 2002, Naumov 2002).

Post-impact mineralization in the Charlevoix impact structure has not been studied, although certain alteration-induced effects have been previously documented by Roy (1979) and Rondot (1989). In this work, Ca-rich zones in crystalline target-rocks from the Charlevoix structure are investigated by optical microscopy, analytical scanning electron microscopy and cathodoluminescence microscopy. The objective is to characterize the nature of the alteration and to provide constraints on conditions during metasomatism.

Geological Setting

The Charlevoix impact structure (47°32'N, 70°18'W), previously known as La Malbaie structure (Robertson 1968), is located ~105 km northeast of Quebec City along the north shore of the St. Lawrence River (Fig. 1). The topographic expression of the ~54-km diameter complex structure remains well defined. The prominent central peak, the Mont des Eboulements, marks the center of the structure. However, the southeastern part of the crater, in the St. Lawrence River, has been obliterated by thrusting along Logan's Line (Robertson 1968). This is a southeast-dipping fault that separates Precambrian Shield units to the northwest from Appalachian units to the southeast (Neale *et al.* 1961, Kumarapeli 1985). The Charlevoix structure lies within the seismically active St. Lawrence rift system, which is interpreted to have been initiated in Neoproterozoic – early Paleozoic times, during opening of the Iapetus Ocean, and reactivated during the Paleozoic and Mesozoic (*e.g.*, Kumarapeli 1985). Mesozoic low-temperature (90–150°C) hydrothermal veins comprising galena, sphalerite, barite and fluorite have been shown to be related to rifting in northeastern North America and reactivation of the St. Lawrence fault system (Carignan *et al.* 1997). However, the microstructural appearance and the mineralogy of these veins are distinct from the Ca-rich zones described here.

The exposed impact-target lithologies are predominantly crystalline rocks of the Grenville Province of the Canadian Shield (Fig. 1). The oldest (Mesoproterozoic) unit comprises migmatitic paragneisses (1379 ± 66 Ma; Frith & Doig 1973) and granitic gneisses, which are well exposed along the shore of the St. Lawrence River. The most common unit is charnockitic gneiss (1080–1513 Ma; Frith & Doig 1973). An anorthosite complex occurs in the outer western part of the structure (1079 ± 22 Ma; Ashwal & Wooden 1983). Smaller anorthositic dykes and veins also penetrate the charnockites. Middle to Late Ordovician arkoses, quartzites, siltstones and limestones (Trenton and Utica formations) of the St. Lawrence Platform outcrop in the annular trough and along the north shore of the St. Lawrence River within the structure, where they reach several hundred meters in thickness (Robertson 1968). These rocks are commonly found brecciated and may exhibit well-developed shatter cones. Stratigraphic and paleogeographic reconstruction indicates that a continuous cover of these sedimentary rocks was present above the crystalline basement at the time of impact (Robertson 1968, Roy 1979, Rondot 1989). The youngest sedimentary rocks of the Utica Formation are flysch, olistostrome and turbidite (Robertson 1968, Rondot 1989). Therefore, lake and marine waters may have been available, in addition to ground water, for a post-shock hydrothermal system.

Structural observations indicate that the impact structure is eroded by at least 1 km (Roy 1979). Virtually all crater-fill deposits have been removed. Impact melt rocks have only been found reworked in glacial debris northeast of the central peak, and in two small outcrops 9 and 10 km from the central peak, which are reported to be in place (Rondot 1971). These outcrops may have been part of a more extensive melt sheet that has since been eroded (Robertson 1968). K/Ar data from these impact-melt rocks imply a formation age of ~357 ± 15 Ma (Rondot 1971). However, new Ar/Ar laser fusion data imply a late Ordovician age for the impact (Whitehead *et al.* 2003). Stratigraphically, the maximum age for the impact is given by the youngest pre-impact deposits of the Utica Formation (~450 Ma; Robertson 1968, Rondot 1989). The crater originated prior to the thrusting of unshocked rocks of the Île-aux-Coudres into the crater region, which obscured the southeastern part of the structure during the Acadian Orogeny (~377 Ma, Robertson 1968, Whitehead *et al.* 1996, Fig. 1). This provides a minimum age of the impact.

There is no evidence for post-impact regional thermal overprinting >300°C in the Charlevoix area. The survival of biotite K/Ar ages of ~900 Ma from the anorthosite complex in the outer western part of the structure (Wanless & Lowdon 1961) indicates that those rocks of the Charlevoix area that were unaffected by shock metamorphism have, since that time, remained below the biotite closure temperature (~300°C, *e.g.*, Hodges 1991).

METHODS

Polished thin sections were prepared from ten hand samples of the Ca-rich zones. The orientations of planar deformation features (PDFs) in shocked quartz were determined using a Leitz U-stage mounted on a Leitz optical microscope. The indexing of different types of PDFs (Engelhardt & Bertsch 1969, Langenhorst 2002) was performed using the computer program StereoNett 2.0 (Duyster 1996).

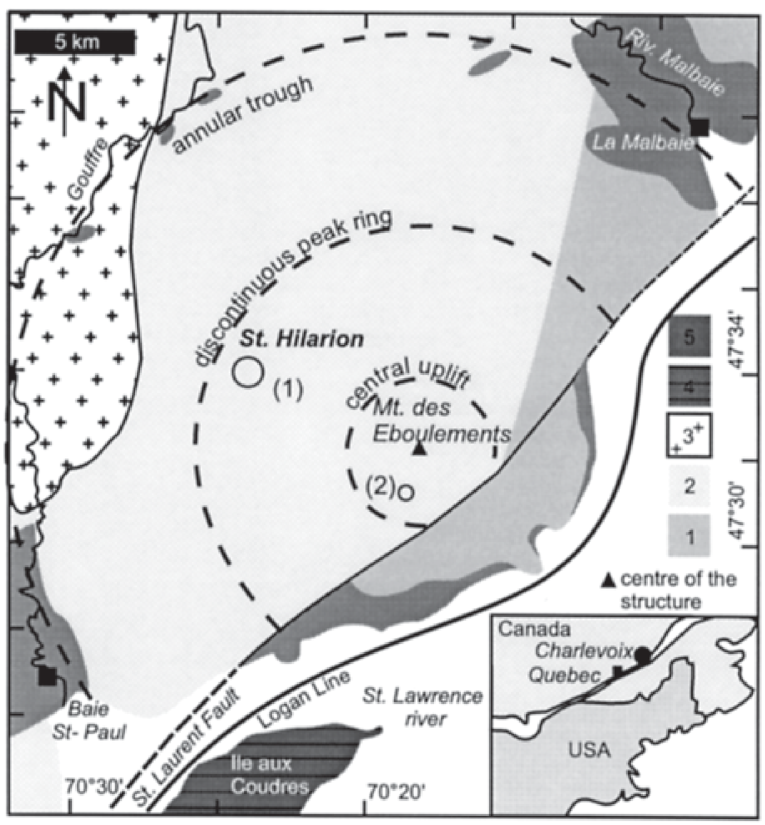


FIG. 1. Simplified geological map of the Charlevoix impact structure. 1: Granitic gneisses and migmatites of the Grenville Province, 2: Charnockitic gneisses of the Grenville Province, 3: Anorthosite of the Grenville Province, 4: Cambrian sedimentary rocks of the Appalachians. 5: Ordovician sedimentary rocks of the St. Lawrence Platform. Black open circles: sample locations 1 and 2.

Microstructure and mineralogy were investigated with a JEOL JSM–6400 scanning electron microscope (SEM) equipped with a Link analytical eXL energy-dispersion spectrometer and a Si(Li) LZ–4 Pentafet detector. This SEM was operated at an accelerating voltage of ~15 kV, a beam current of ~1.5 nA and a working distance of 39 mm. Analytical results were calibrated using a multi-element standards block (Type 202–52) produced by the C.M. Taylor Corporation of Sunnyvale, California, USA.

Cathodoluminescence (CL) microscopy proved to be a powerful tool for distinguishing shocked remnant quartz of the host gneisses from unshocked secondary quartz in the Ca-rich zones, and for recognition of phases within fine-grained cataclastic zones. It is difficult to interpret CL differences quantitatively (Marshall 1988). However, it is a complementary technique, as information can be obtained on internal structure and lattice defects not discernible by other analytical methods (Zinkernagel 1978, Marshall 1988, Götze *et al.* 2001). CL imaging was performed on a "cold cathode" luminoscope (University of New Brunswick, Fredericton) operated at 10–12 kV and 0.6–0.8 mA. CL spectra were measured on a "hot cathode" microscope (HC1–LM, Ruhr-University, Bochum) using a digital spectrograph with CCD detector at a wavelength range from 320 to 800 nm at standardized conditions (wavelength calibration with Hg). The CL spectra were recorded at an acceleration voltage of 14 kV, a beam current (density) of 0.2 mA, and an integration time of 20 s. CL analysis was carried out on polished and carbon-coated thin sections.

The subgrain structure and the crystallographic misorientation of quartz crystals were investigated by electron-back-scatter diffraction (EBSD) using a LEO 1530 SEM equipped with field emission gun and forescatter detector (Ruhr-Universität Bochum, Germany). The EBSD technique provides the full crystallographic orientation of crystals in a thin section using a back-scattered-electron (BSE) signal (*e.g.*, Lloyd 1987, Prior *et al.* 1996, 1999). It was complemented by orientation contrast (OC)-imaging, another SEM-based technique, which reveals crystallographic misorientation between adjacent grains by grey-scale contrast. Although this contrast does not correlate with the magnitude of misorientation, OC images provide information on the shape of grain boundaries. The thin sections for EBSD were chemically polished with a colloidal silicon suspension (SYTON®) to minimize surface damage, and then coated with carbon to limit charging effects. For EBSD analysis, this SEM was operated at an accelerating voltage of 25 kV and a working distance of 25 mm, with the section tilted at an angle of 70° with respect to the beam, to optimize the BSE signal.

Field Setting and Determinations of Peak-Shock Pressure

The Ca-rich zones occur as oblate spheroid lenses up 0.5 m in diameter, and as planar veins up to 0.5 m wide. They contrast with the host gneisses in being lighter and white-grey in color and in containing cm-scale cavities and vugs (Figs. 2a–c, 3). The occurrence of these zones is sporadic. They are commonly developed in the core region of the impact structure (*i.e.*, within 10–15 km radius of its center). The Ca-rich zones depicted in Figure 3 are "end members"; transitions between the lensoid and vein forms also occur.

Ca-rich zones were investigated in detail at two locations (Fig. 1): (1) southeast of the village St. Hilarion, ~8 km distance from the central peak (coordinates 47°33.844'E, 70°22.861'W), and (2) southeast of, and ~0.5 km from, the central peak (coordinates 47°31.579'E, 70°17.484'W). At both locations, the host charnockitic gneiss consists of quartz, plagioclase, K-feldspar and rare clino- and orthopyroxene, as well as accessory magnetite, ilmenite, titanite, zircon and apatite. The pyroxenes are partly altered to amphibole owing to pre-impact retrograde metamorphism (Rondot 1989).

At location 1, several lensoid Ca-rich zones occur in strongly fractured charnockitic gneiss. The gneiss is typically comminuted at the contact with the metasomatic lenses (Figs. 2a, b, 3a). The host gneiss contains well-developed shock features in the form of shatter cones and planar deformation features (PDFs) in quartz (Fig. 4). The abundance of different sets of PDFs can be used to give an estimate of the shock pressure (*e.g.*, Robertson & Grieve 1977, Stöffler & Langenhorst 1994). According to U-stage measurements, most quartz crystals in charnockitic gneiss at location 1 contain only PDFs parallel to the basal plane (0001) (54%), ~38.5% of the grains contain rhombohedral PDFs parallel to {103}, and a few crystals (7–8%) show, in addition, PDFs parallel to {101}, {112} or {221} planes (Fig. 4c). Grains containing PDFs parallel to {102} rhombohedra were not observed. Using the calibration scheme of Robertson & Grieve (1977), this abundance of PDF features indicates that these rocks experienced shock pressures of ~9 GPa (Robertson 1975, Trepmann & Spray 2005).

Location 2 reveals an occurrence of a Ca-rich vein (Fig. 3b), which is oriented parallel to the well-developed foliation of the highly shocked host charnockitic gneiss (Figs. 5, 6a). Within this Ca-rich zone, the foliation is still preserved by elongate quartz crystals (Fig. 5). Elongate, open cavities are aligned with their long axes in the foliation plane (Fig. 3b). In the host gneiss at this location, ~64% of the grains contain PDFs parallel to {103} rhombohedra and ~46% of the grains contain, in addition, PDFs parallel to the {102} rhombohedra, as revealed by U-stage measurements (Fig. 5d). This abun-

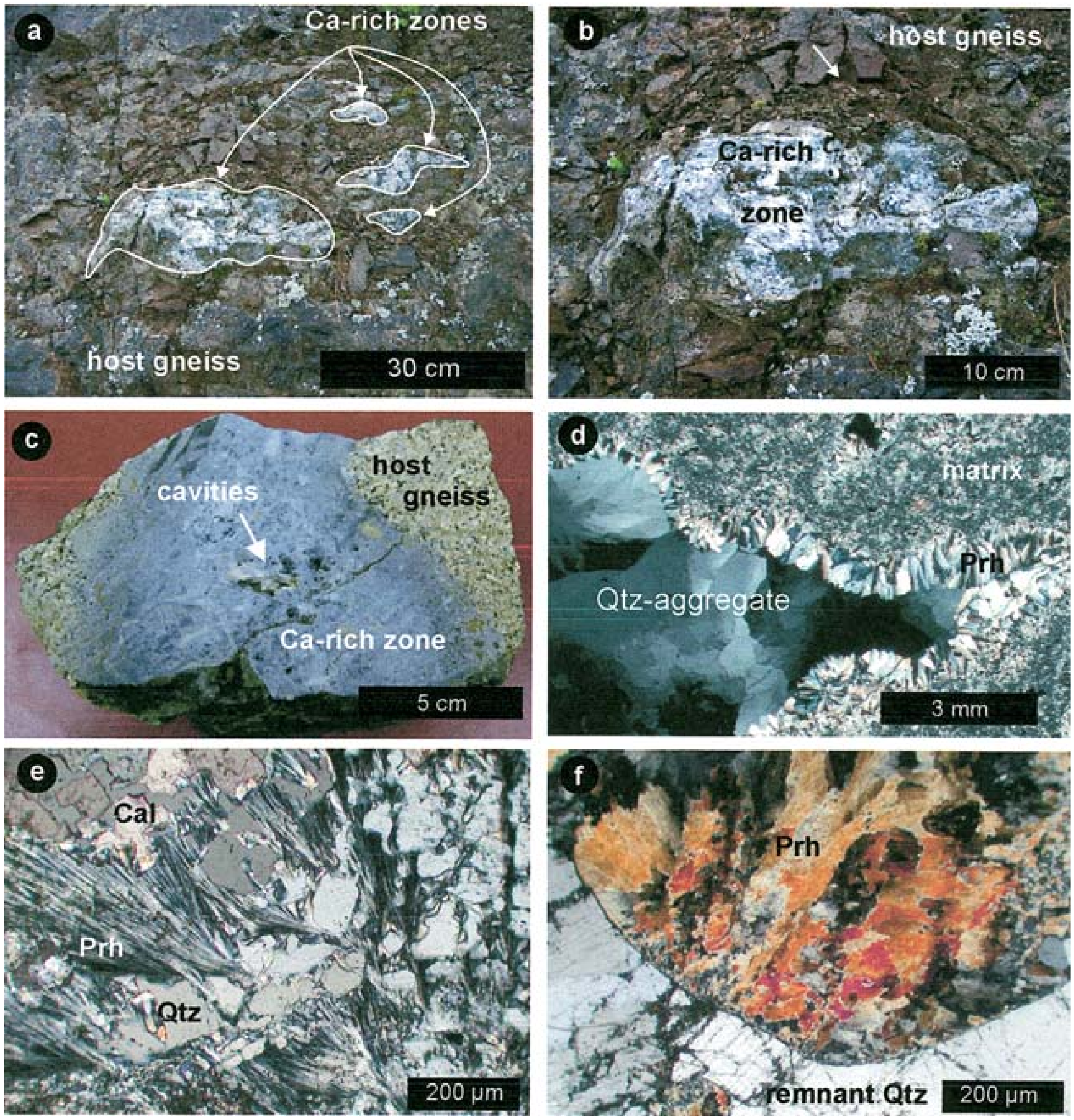


FIG. 2. Ca-rich zones in host charnockites from location 1. (a), (b) Field photographs showing Ca-rich zones that contain cavities. Note comminuted gneiss at the contact with the Ca-rich zone, marked by an arrow in (b). (c) Hand sample comprising a Ca-rich zone containing cavities at the contact with the host gneiss. (d) Photomicrograph (cross-polarized light) of quartz aggregate surrounded by coarse-grained prehnite. Quartz and prehnite show a fibrous subgrain structure. This feature is interpreted as a mineralized cavity. (e) Photomicrograph (cross-polarized light) of coarse-grained prehnite and calcite with clasts of relict shocked quartz. (f) Photomicrograph (cross-polarized light) of curved interface of prehnite adjacent to relict shocked quartz.

dance of characteristic sets of PDF features implies shock pressures of ~13 GPa (Robertson 1975, Robertson & Grieve 1977, Trepmann & Spray 2005).

We note that location 2 occurs in the central uplift of and closer to the center of the structure than location 1, which is in keeping with a radial decrease in recorded peak shock pressure (*i.e.*, ~13 GPa at 0.5 km from the structure's center, *versus* 9 GPa 8 km away).

Mineralogy and Microstructure of the Ca-Rich Zones

The mineralogy and microstructure of the Ca-rich zones have been investigated in nine samples from location 1 and in one sample from location 2. The Ca-rich zones from both localities consist mostly of prehnite (50–80%), quartz (30–50%) and calcite (0–10%). These phases constitute a fine-grained (20–50 μm) matrix, or form larger mm-size grains (Figs. 2d–f). The Fe content of prehnite in different grains varies from 1 to 9 wt.% Fe_2O_3 (Table 1). With increasing Fe content, the $^{[6]}Al$ content decreases, indicating Fe^{3+} substitution for Al^{3+} (Deer *et al.* 1992). Generally, finer-grained prehnite in the matrix is lower in Fe, characterized by a light yellow CL, compared to coarser-grained prehnite, which shows no luminescence owing to its higher Fe content (Figs. 6a, b). The calcite is pure $CaCO_3$.

Two generations of quartz can be distinguished in the Ca-rich zones: (1) quartz crystals in aggregates (grain size 100–200 μm), which exhibit no shock effects and no visible CL, or a dark brown CL (Figs. 2d, 5b, c, 6a, b). Locally, these quartz crystals are idiomorphic with well-developed rhombohedral faces (Figs. 5b, c). This quartz is secondary. (2) Large (grain size >1 mm) single crystals of quartz showing abundant PDFs and a bright blue luminescence (Fig. 6). These show the same characteristics as shocked quartz from the host charnockitic gneiss. The shocked single crystals of quartz may show amoeboid or curved interfaces with the prehnite matrix (Fig. 2f). This quartz is considered relict (*i.e.*, it formed prior to impact and metasomatism).

Secondary quartz with rhombohedral crystal faces has, in places, grown epitactically onto shocked quartz (Fig. 5c). Small (~50–100 μm) globular, blue-luminescing quartz crystals can occur within weakly luminescent quartz aggregates (Figs. 6a, b). The aggregates are commonly surrounded by coarse-grained prehnite, forming irregular blebs several millimeters in diameter within the fine-grained matrix (Fig. 2d). Prehnite and quartz in these blebs show a fibrous subgrain structure. Secondary quartz also may exhibit a spherulitic substructure, with most subgrains having a misorientation angle (uncorrelated) of <3°; however, the misorientation angle may attain 10° (Fig. 7).

The blue luminescence of shocked quartz is more intense than in quartz crystals apparently devoid of shock effects in charnockitic gneiss from the periphery of the impact structure. The latter show a dark violet

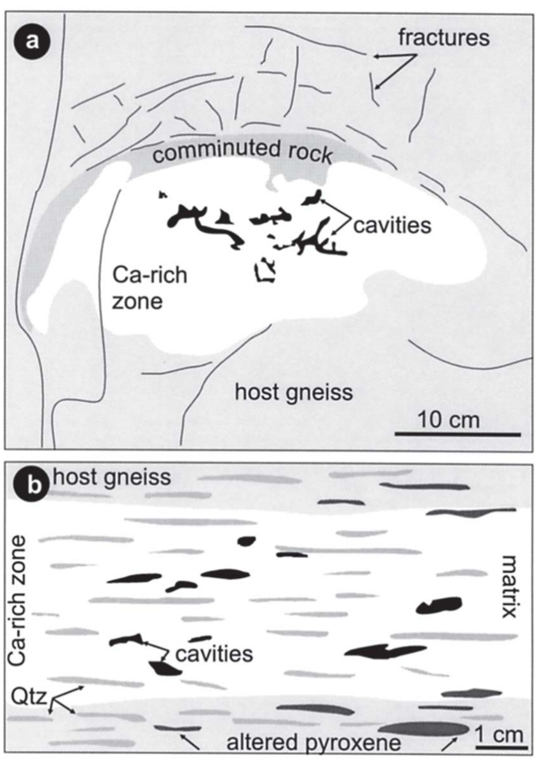


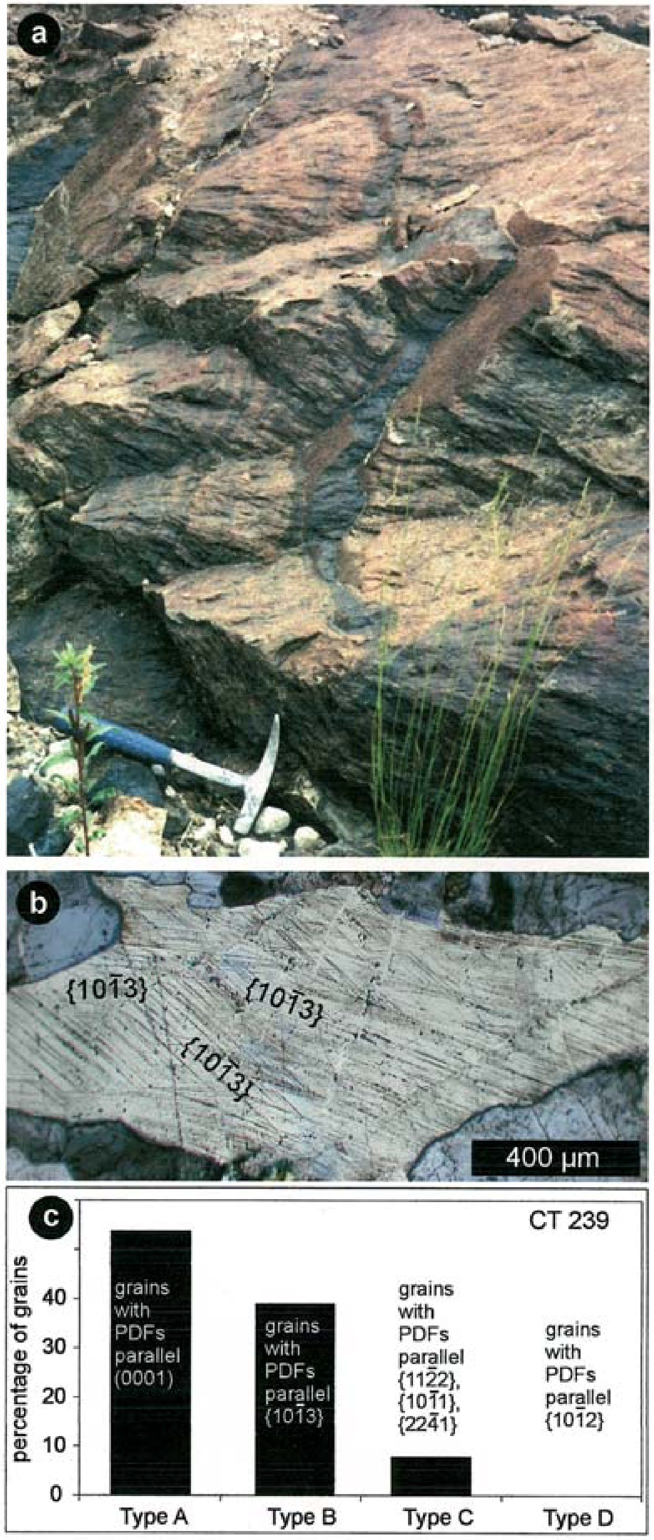
FIG. 3. Simplified diagrams of Ca-rich zones within host gneisses. (a) Lensoid Ca-rich zones from location 1; compare Figure 2b. (b) Vein-like Ca-rich zone from location 2.

TABLE 1. REPRESENTATIVE COMPOSITIONS OF PREHNITE FROM LOCATION 1 AND 2, CHARLEVOIX STRUCTURE

SiO_2 wt%	43.95	44.47	43.53	41.66
Al_2O_3	23.34	23.60	20.08	18.79
Fe_2O_3*	1.18	1.42	7.25	9.04
CaO	26.21	26.88	26.36	25.92
K_2O	0.30	0.00	0.00	0.00
H_2O	5.01	3.63	2.79	4.59
Total**	100.00	100.00	100.00	100.00
Si *apfu*	6.01	6.08	5.95	5.70
$^{[4]}Al$	1.99	1.92	2.05	2.30
$^{[6]}Al$	1.77	1.89	1.19	0.73
Fe^{3+}	0.12	0.15	0.75	0.93
Ca	3.84	3.94	3.86	3.80
K	0.05	0.00	0.00	0.00
H	4.57	3.31	2.54	4.19

* all iron as Fe_2O_3. ** Summed to 100%, with the difference attributed to H_2O. The proportion of cations is calculated on the basis of 24 atoms of oxygen, and quoted in atoms per formula unit (*apfu*).

FIG. 4. Shock features in charnockitic gneisses from location 1. (a) Field photograph showing well-developed shatter cones. (b) Different sets of planar deformation features in quartz. (c) Histogram of percentage of quartz grains with characteristic sets of planar deformation features, indicating a shock pressure of ~9 GPa.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grains with PDFs parallel (0001)
grains with PDFs parallel {10$\bar{1}$3}
grains with PDFs parallel {11$\bar{2}$2}, {10$\bar{1}$1}, {22$\bar{4}$1}
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Type A
Type B
Type C
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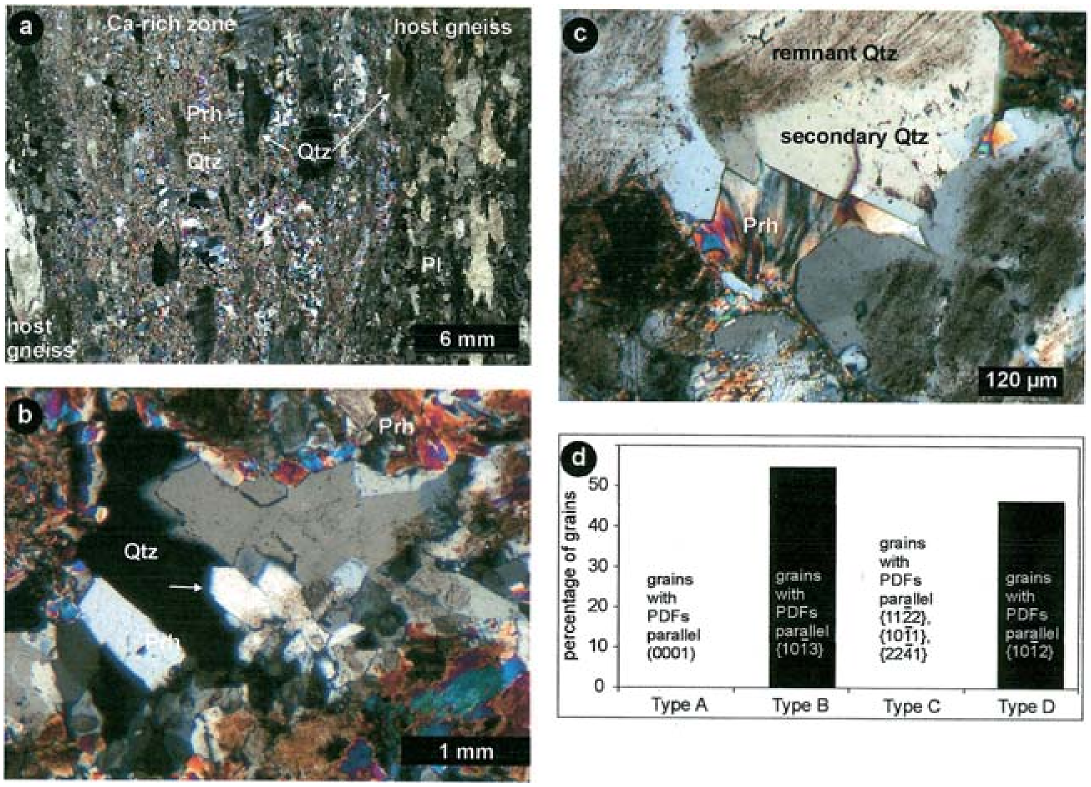


FIG. 5. (a–c) Photomicrographs (cross-polarized light) showing Ca-rich zone from location 2. (a) Ca-rich zone (left) mainly comprises prehnite, secondary quartz and relict shocked quartz. Adjacent host gneiss (right) comprises mainly quartz and plagioclase. (b) Quartz in aggregate shows idiomorphic shape of crystals (arrow), indicating unconfined crystallization from a fluid. (c) Idiomorphic crystals of secondary quartz that have grown epitactically onto relics of shocked (PDF-bearing) quartz. (d) Histogram of percentage of quartz grains with characteristic sets of planar deformation features, indicating a shock pressure of ~13 GPa.

luminescence. However, in CL emission spectra, shocked and unshocked quartz show very similar bands, with peaks at ~443 and ~500 nm, which are common for quartz of plutonic origin (Götze *et al.* 2001). These bands are probably due to intrinsic defects, as observed in several oxygen-based minerals (Habermann *et al.* 1999). The CL emission spectra of shocked quartz exhibit an additional broad band with a maximum at approximately 630 nm (Fig. 6c). This band is commonly assigned to non-bridging oxygen hole centers (NBOHC, *e.g.*, Stevens *et al.* 1995), which might be amplified by shock. Changes in CL properties in experimentally shocked quartz have been reported by Gucsik *et al.* (2003).

The fact that the quartz single-crystal clasts show the same characteristics (grain size, blue luminescence and PDFs) as quartz from the charnockitic gneiss confirms that they are inherited from the host rock. The same holds true for clasts of feldspar, pyroxene or amphibole, K-feldspar, zircon, magnetite, titanite and ilmenite that occur in the Ca-rich zones (Figs. 8, 9). They are constituents of the charnockites, and show similar compositions and, if not fragmented, comparable grain-sizes. They occur commonly at the contact with the host gneiss within fine-grained (<10 µm) cataclastic zones of several millimeters to 1 cm in total thickness (Fig. 8). Zircon, magnetite, titanite and ilmenite within the Ca-rich zones are especially commonly cataclastically deformed (Fig. 9). Feldspar and pyroxene or amphibole clasts are rare and restricted to the fragmented margins (contact zone with the host gneiss). Plagioclase is absent in the Ca-rich zones from location 2, although both quartz and plagioclase are the main phases in the host gneiss (Fig. 5a).

The abundance of remnant clasts in Ca-rich zones is variable. In the vein-like Ca-rich zone of location 2, remnant quartz is very common, comprising ~10–20% of the phases present. In the lensoid Ca-rich zones of location 1, remnant phases are typically less abundant (<10%), and zircon, magnetite, titanite and ilmenite

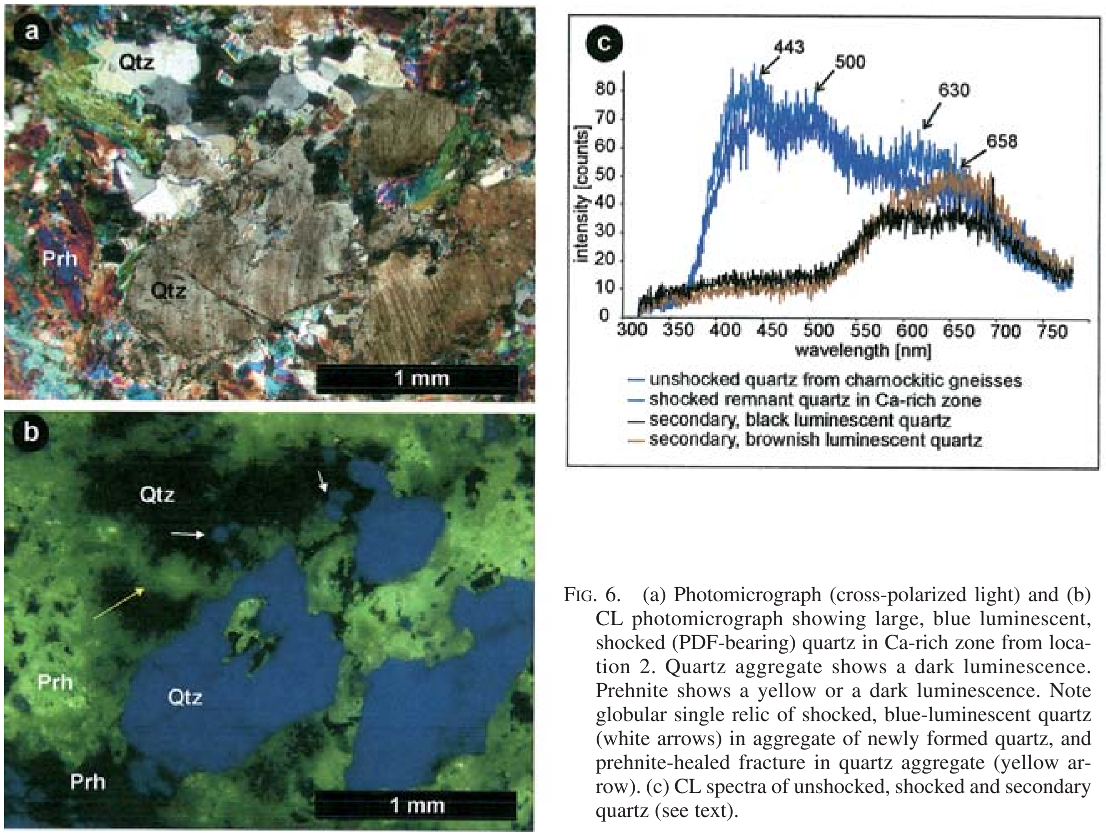


FIG. 6. (a) Photomicrograph (cross-polarized light) and (b) CL photomicrograph showing large, blue luminescent, shocked (PDF-bearing) quartz in Ca-rich zone from location 2. Quartz aggregate shows a dark luminescence. Prehnite shows a yellow or a dark luminescence. Note globular single relic of shocked, blue-luminescent quartz (white arrows) in aggregate of newly formed quartz, and prehnite-healed fracture in quartz aggregate (yellow arrow). (c) CL spectra of unshocked, shocked and secondary quartz (see text).

occur in volumes equal to, or greater than, that of remnant quartz.

DISCUSSION

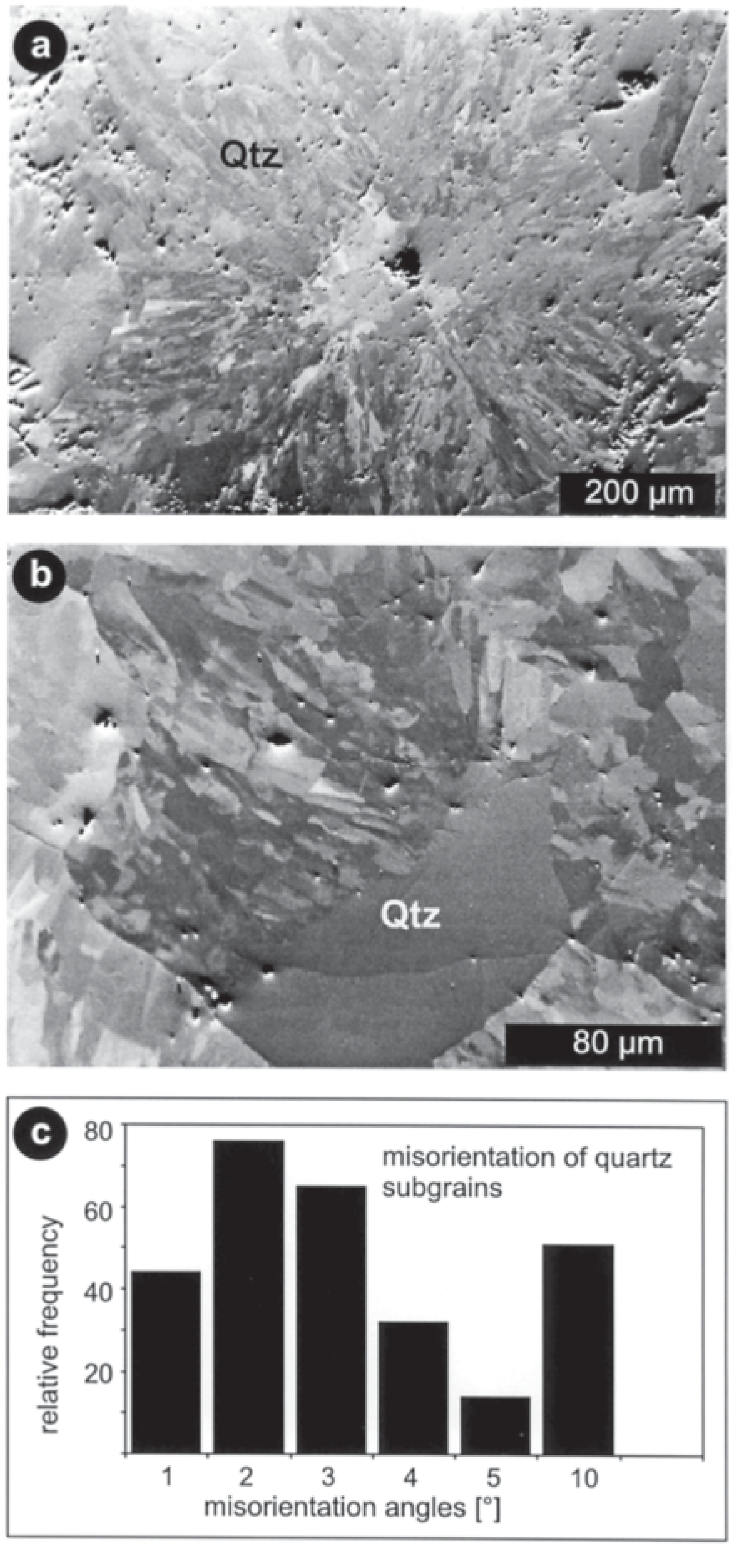
Metasomatic phases

Prehnite, calcite and unshocked quartz are interpreted to be of metasomatic origin. The low intensity of the luminescence of the aggregates of metasomatic quartz (Figs. 2d, 6) indicates only very few point defects, which supports an authigenic (post-impact) origin (Götze *et al.* 2001). An internal structure in the quartz aggregates is visible in the CL microscope as dark luminescent grains surrounded by dark brownish luminescent quartz, characterized by a broad band in the CL emission spectra with a peak at ~658 nm (Fig. 6c). This could be an expression of a temporal evolution from a nearly defect-free crystallization to a more rapid, but still defect-poor, crystallization during precipitation.

Irregular blebs of quartz aggregates surrounded by coarse-grained prehnite embedded in a fine-grained prehnite-rich matrix (Figs. 2d, 5b) are interpreted to be filled cavities, as supported by the locally idiomorphic shape of the crystals (Fig. 5b). We propose that coarse-grained prehnite crystallized first at the interface of a cavity bordered with a prehnite-rich matrix (Fig. 2d). Subsequently, quartz filled the remaining pore-space. Prehnite-and quartz-filled cavities within the Ca-rich zones that are themselves cross-cut by prehnite-filled fractures (Figs. 6a, b) imply successive episodes of precipitation.

Temperatures of metasomatism and the source of heat

The replacement of shocked quartz by newly crystallized quartz, which shows no shock effects (Figs. 6a, b), provides clear evidence that the metasomatic event occurred after impact. Microthermometric data from fluid inclusions aligned in PDFs in shocked quartz from Charlevoix reveal evidence for the circulation of a hot aqueous fluid at initial temperatures of >500°C and at atmospheric pressure (Pagel & Poty 1975). This is consistent with the development of Dauphiné twins associated with PDFs and the crystallographic orientation of associated planar microstructures, which together indicate that temperatures must have attained at least 573°C shortly after impact (Trepmann & Spray 2005).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Qtz
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b
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misorientation of quartz subgrains
relative frequency
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10
misorientation angles [°]

Prehnite, as the main constituent, indicates that the temperature of the fluid responsible for the Charlevoix metasomatism was at 250–380°C at pressures ≤300 MPa (Liou 1971, McCarville & Crossey 1996). The fibrous and spherulitic subgrain structure of quartz in aggregates of the lensoid Ca-rich zones from location 1 (Figs. 2d, 7a, b) is characteristic of lower temperatures (Frondel 1978, Graetsch 1994), suggesting subsequent crystallization at <180°C (Arnorsson 1975, McCarville & Crossey 1996). The above constraints indicate an impact-related hydrothermal system operating from ~600°C down to ~100°C, consistent with the restriction of the Ca-rich zones to the impact structure.

Sources of energy for driving a post-shock hydrothermal system include: (1) development of an overlying superheated impact-melt sheet with hot fallback, (2) elevated geotherms owing to formation of a central uplift, and (3) liberation of waste heat from shock-wave passage (*e.g.*, Naumov 2002, Osinski *et al.* 2001, Turtle *et al.* 2003).

Structural observations at Charlevoix indicate a maximum elevation of central uplift rocks of ~6 km (Roy 1979). At the time of impact, the Charlevoix area was tectonically active owing to the ongoing Taconic orogeny. Assuming an average geothermal gradient of ~30 km^{-1} and removal of ~1 km of material since the impact event (Robertson 1975, Roy 1979), temperatures of ~200°C are expected from elevated geotherms. Because the Charlevoix structure is eroded, with most crater-fill products having been removed, it is not possible to confirm whether an overlying melt-sheet might have acted as an additional source of heat for the hydrothermal system. However, based on the size of the transient cavity at Charlevoix, the presence of a melt sheet and fallback is considered highly likely (Melosh 1989). Therefore, additional heat (to attain initial temperatures of up to 600°C) is considered to have come from the presence of an overlying impact-melt sheet and accompanying hot fallback, as well as from waste heat released by shock-wave decompression.

Metasomatic influx and replacement processes

Because of heterogeneity in the abundance of metasomatic phases in the Ca-rich zones, coupled with a varying abundance of remnant clasts from the host gneiss, representative bulk-compositions of the Ca-rich zones cannot be obtained. It is also difficult to determine the composition of the metasomatizing fluid. The absence of plagioclase in the Ca-rich zone from location 2 (despite its abundance in the host gneiss, Fig. 5a) and the survival of remnant shocked quartz, suggest that the source fluid reacted selectively with plagioclase and so replaced the anorthite component. A reaction describing this has been reported by McCarville & Crossey (1996, their reaction 3):

$$\underset{\text{anorthite}}{CaAl_2Si_2O_8} + Ca^{2+} + H_4SiO_4 \Rightarrow \underset{\text{prehnite}}{Ca_2Al_2Si_3O_{10}(OH)_2} + 2\,H^+ \quad (1)$$

The presence of the iron-dominant component of prehnite, especially in the coarser-grained occurrences, also requires iron to have been in solution. A reaction depicting the hydrolysis of primary magnetite, abundant in the charnockitic gneisses, to form dissolved Fe^{3+} might be:

$$\underset{\text{magnetite}}{2Fe_3O_4} + 18\,H^+ + \tfrac{1}{2}\,O_2 \Rightarrow 6\,Fe^{3+} + 9\,H_2O \quad (2).$$

However, it is not possible to estimate to what extent primary phases from the host gneiss may have been dissolved and replaced. Given the relatively Ca-poor composition of the host charnockitic gneiss (Table 2), the volume of prehnite (with 26–27 wt.% CaO, Table 1) cannot be explained by a replacement of the anorthite component of host-rock plagioclase alone. This, and the occurrence of secondary calcite, suggests the need for an external source of Ca^{2+} and CO_2, which may have been the carbonaceous Ordovician target-rocks overlying the Grenvillian basement at the time of impact. On the other hand, Si, Al and Fe^{3+} could have been derived mainly from the reaction of the fluid with the host gneiss.

Considerations of permeability and porosity

The sporadic occurrence of both the oblate- and vein-type Ca-metasomatic zones and the lack of evidence for pervasive hydrothermal alteration in the target rocks indicate a highly focused metasomatic process. Although the target rocks do exhibit impact-induced fracturing (Robertson 1968, Rondot 1989), it is noteworthy that the host gneiss is more intensely fractured directly adjacent to the Ca-rich zones (Figs. 2a, b, 3a). Moreover, the inherited clasts of the host gneiss are commonly cataclastically deformed at these contacts (Figs. 8, 9). These observations suggest two possible mechanisms for Ca-rich zone generation:

(1) Bulk permeability in the host rocks was enhanced by impact-induced fracturing. Localized cataclastic deformation and enhanced porosity at the site of Ca-zone formation was subsequently caused by hydrofracturing.

FIG. 7. (a) Orientation-contrast image reveals a spherulitic subgrain structure of quartz in aggregates in Ca-rich zones from location 2, which is characteristic of low-temperature crystallization in open pore-space. (b) Orientation-contrast image of quartz in aggregate shows a partly homogeneous orientation and a partly fibrous subgrain structure. (c) Histogram of misorientation angles (uncorrelated) of subgrains in (b), derived from manual EBSD measurements.

Cataclasis of the host gneiss at contacts with the Ca-rich zones is due to increased fluid pressure that facilitated brittle failure. The occurrence of cavities and vugs was caused by the subsequent release of volatiles from the fluid by decompression or boiling. This origin for the Ca-rich zones requires extreme local excursions in fluid pressure into highly porous and permeable sites.

(2) Localized cataclastic deformation and enhanced permeability in the host gneiss is impact-induced. Whereas the bulk rock is fractured as a result of shock-wave passage, and so is rendered permeable, there needs to be a mechanism for generating localized zones of more intense fragmentation where fluids can accumulate and precipitate new minerals. Such repositories may be generated by interference effects between shock wave and the rock if discrete volumes of rock are imploded or exploded, or where slip systems intersect. The prevalence of comminuted margins of the metasomatic zones suggests that a degree of displacement (*i.e.*, faulting) may have been involved in their generation. Similar mineralization effects in cavities following fluid infiltration into a host rock with a high impact-induced porosity are described from the Manson impact structure, in Iowa (McCarville & Crossey 1996). Localization of impact-induced hydrothermal alteration along pipes in concentric systems of faults at the Haughton impact crater has been reported by Osinski *et al.* (2001). It is also possible that a combination of these two processes took place.

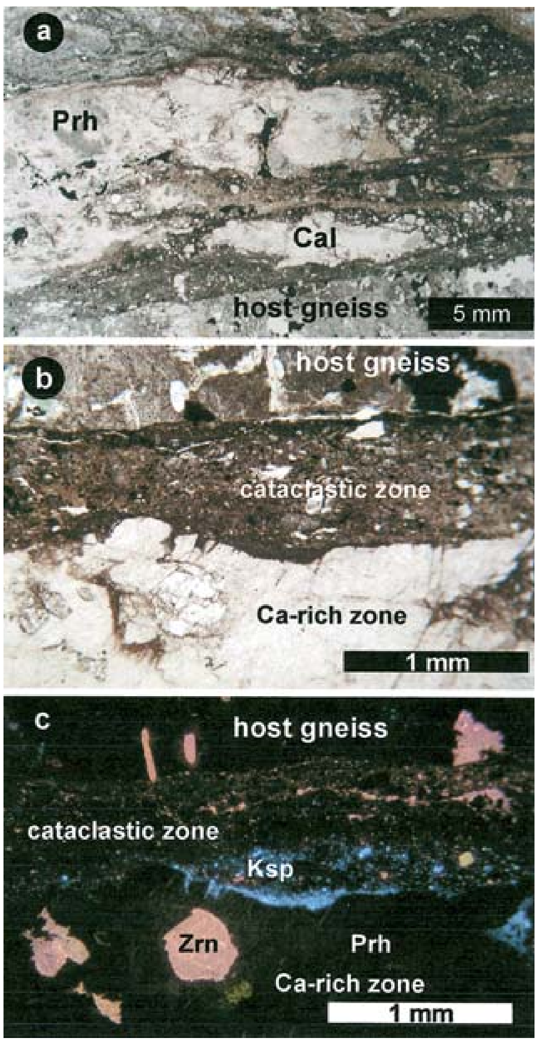

FIG. 8. (a) Photomicrograph (plane-polarized light) showing cataclastic zones in Ca-rich zone from location 2 at contact with host gneiss. (b) Optical (plane-polarized light) and (c) CL photomicrograph exhibiting cataclastic zone comprising K-feldspar (lightly blue-luminescent) and zircon (pink-luminescent). Prehnite from the Ca-rich zone is not luminescent.

CONCLUSIONS

The development of Ca-rich metasomatic lenses and veins in charnockitic gneisses of the Charlevoix impact structure is attributed to mineralization by hydrothermal fluids in intensely fragmented zones that were generated locally by hydrofracturing and impact-induced cataclasis. The predominant paragenesis is prehnite + quartz ± calcite. Given the Ca- and CO_2-poor composition of the host gneiss, carbonaceous Ordovician rocks overlying the Grenvillian basement at the time of impact might have acted as an external source for these components. Silicon, Al and Fe^{3+} were probably derived by the reaction of the fluid with the host gneisses, which is apparent by a partial replacement of shocked quartz by secondary authigenic quartz aggregates. Prehnite probably grew at the expense of the anorthite component of the host plagioclase. The predominance of prehnite indicates that precipitation mainly took place at 250–380°C, probably following a higher-temperature phase (>500°C) recorded by fluid inclusions trapped within PDFs in shocked quartz shortly after impact (Pagel & Poty 1975). Mineralized cavities within the Ca-rich zones are themselves cross-cut by prehnite-filled fractures, and quartz partly shows a fibrous or

TABLE 2. WHOLE-ROCK COMPOSITION OF CHARNOCKITIC GNEISS, CHARLEVOIX STRUCTURE

SiO_2 wt%	66.42	MnO	0.08	P_2O_5	0.19
TiO_2	0.69	MgO	0.93	CO_2	0.19
Al_2O_3	14.34	CaO	2.04	H_2O*	1.35
Fe_2O_3	1.67	Na_2O	3.11		
FeO	3.27	K_2O	5.90	Total	100.18

* Loss on ignition. The composition is taken from Rondot (1989).

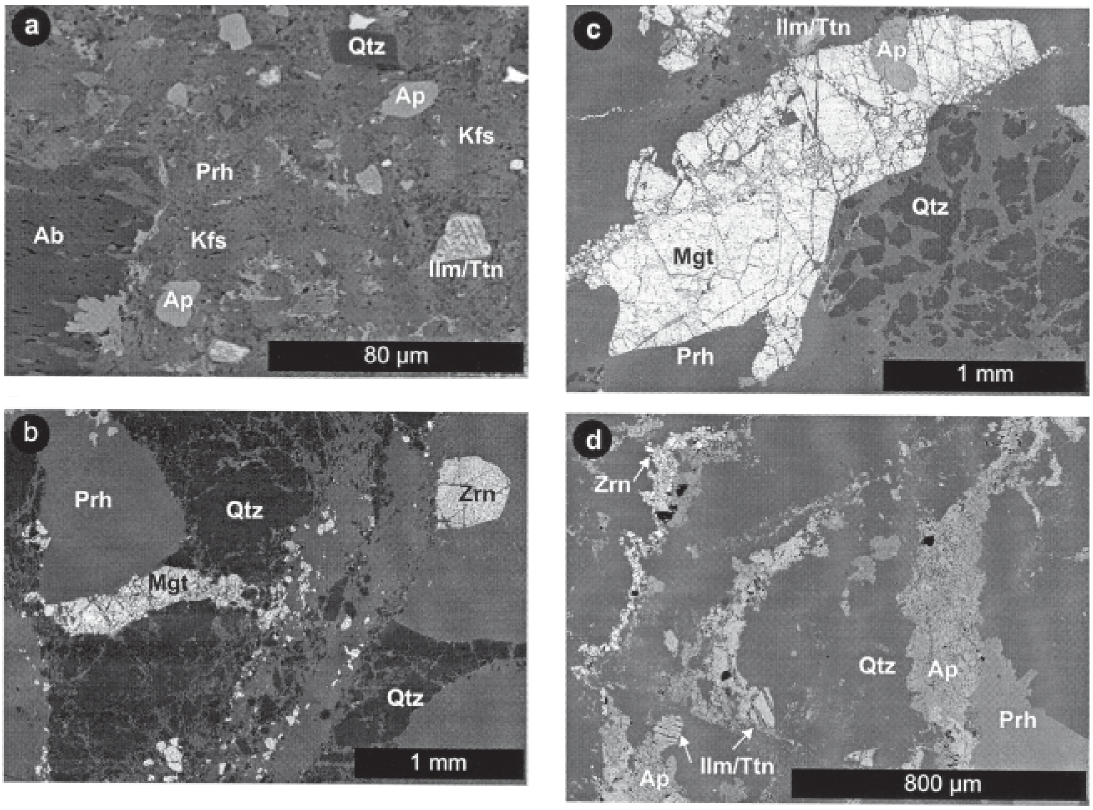

FIG. 9. BSE images of Ca-rich zone from location 2. (a) Fine-grained cataclastic zone. (b), (c) Cataclastically deformed crystals in matrix of Ca-rich zone. (d) Cataclastically deformed crystals in quartz-rich aggregate.

spherulitic structure, indicating successive stages of precipitation during cooling. Creation of a sheet of superheated impact-melt with overlying fallback, formation of a central uplift, and waste shock-induced heat together are considered to have provided the thermal energy to drive hydrothermal circulation and metasomatism. A short-lived (<1 Ma) thermal convection of fluid through shock-heated target-rocks along impact-induced fissures with subsequent precipitation into open cavities can explain the occurrence of discrete Ca-rich metasomatic zones at Charlevoix.

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