

Alteration of detrital sphene in sandstone

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In the Upper Proterozoic sandstones of the Brøttum Formation in the Sparagmite Region of southern Norway, detrital sphene has been substantially to completely eliminated through diagenetic decomposition into pseudomorphs of anatase (or, less commonly, rutile) as well as calcite and/or quartz. Evidence for a sphene precursor include the overall shape and mineralogy of the pseudomorphs and the presence of sphene relicts. Moreover, the latter reveal a chemical composition which is similar to that of sphene in the granitic source rocks. Formation of secondary sphene during the lower greenschist metamorphism of the Brøttum Formation has in many instances, particularly with increase of metamorphic grade, occurred at the expense of the pseudomorphs mentioned above. However, in the "lowermost" greenschist facies, secondary sphene has most commonly crystallized from pore fluids or formed by decomposition of detrital Fe-Ti oxides and biotite.

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Introduction

The rarity of detrital sphene in sandstones (Deer et al. 1982) has commonly been attributed to its mechanical instability (hardness 5.0–5.5) that results in its elimination during transportation and reworking at the sites of deposition (e.g., Pettijohn 1975). Yurkova (1970) observed that detrital sphene in sandstones from north Sakhalin (U.S.S.R.) has been broken into small fragments and subsequently has been replaced by leucoxene films. Recently, Morton (1984) suggested that detrital sphene in Tertiary sandstones from the North Sea is altered merely by postdepositional leaching. Investigations of Ordovician limestones of the Kingstone area, Canada (Corlett & McIlreath 1974) and Proterozoic sandstones of the Visingsö Group, Sweden (Morad & AlDahan 1985) conclude that detrital sphene was altered diagenetically into pseudomorphs composed of Ti-oxides as well as quartz and/or calcite. However, these studies have not established further petrological applications of the controlling equilibrium reaction $\text{Ti-oxide} + \text{calcite} + \text{quartz} = \text{sphene} + \text{CO}_2$. Such applications are facilitated by sandstones of the Brøttum Formation because they contain secondary sphene. Hence, direct observations on the equilibrium reaction can be made. The aim of this paper is to provide systematic mineralogical and chemical data on altered detrital sphene and to elucidate conditions of alteration and neof ormation.

The sandstones investigated (more than fifty fresh road-cut samples) are from the Brøttum Formation, Upper Proterozoic, the Sparagmite Region of southern Norway (Fig. 1). The formation represents

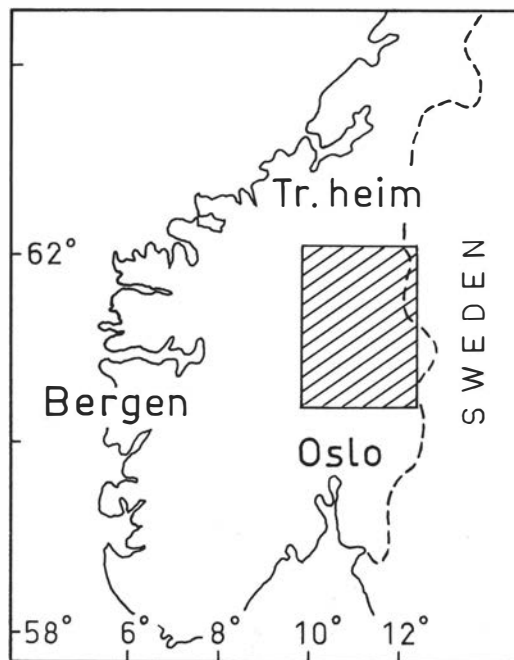


Fig. 1. Location map of the study area.

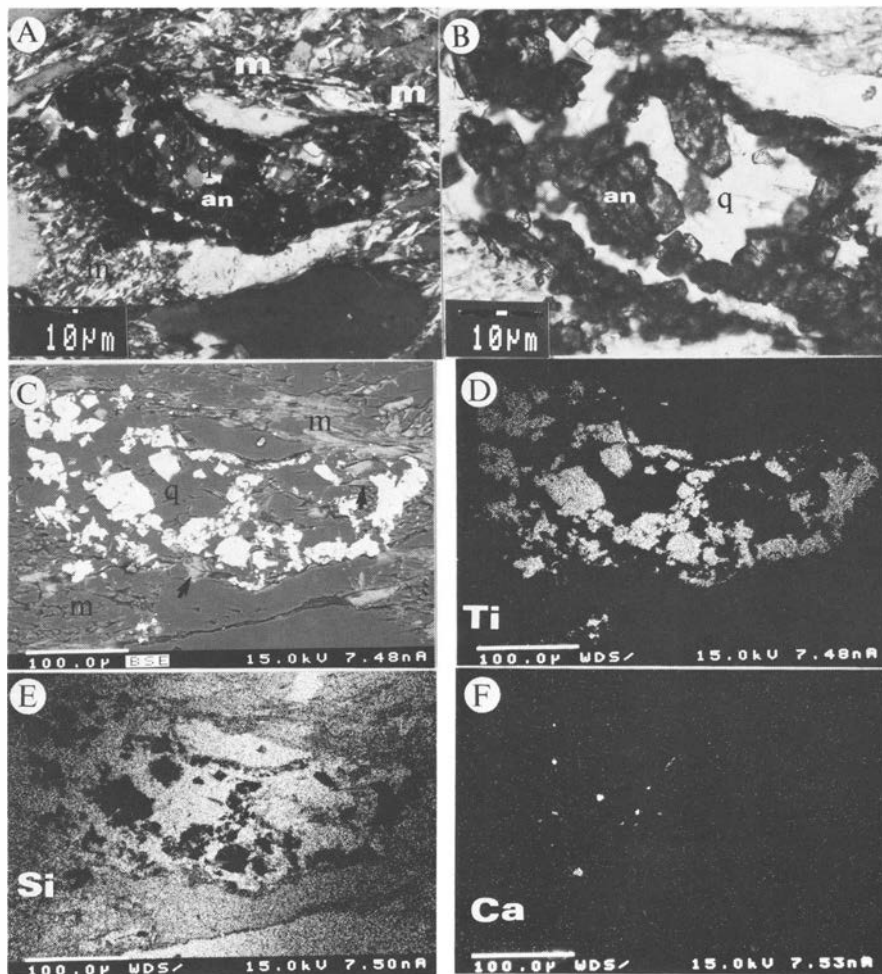


Fig. 2. A pseudomorph of fine-crystalline quartz and anatase.

(A) Photomicrograph (+ nic.) showing a microveinlet-like nature of anatase (an and dark areas) and the occurrence of quartz mainly as numerous crystals (q and greyish areas).

(B) Enlarged view of area outlined in micrograph 2A showing the presence of euhedral anatase crystals intimately intergrown with quartz.

(C) BSE image further revealing the intimate intergrowth of anatase (light) and quartz (light grey) shown in micrograph 2A; arrows show the presence of chlorite in the pseudomorph.

(D-F) X-ray scanning micrographs of Ti, Si and Ca, respectively of the pseudomorph in micrograph 2A.

a thick (>2000 m) sequence of sandstones (graded-bedded, light to dark grey) interbedded with dark grey to black shales which were deposited by submarine fans. The formation has undergone somewhat variable degrees of lower greenschist metamorphism with metamorphic grade increasing in the NW. The increasing metamorphic grade has resulted in the following phyllosilicate assemblages: chlorite + phengite; chlorite + phengite + stilpnomelane; chlorite + phengite + stilpnomelane + bio-

tite; and, less commonly, phengite + biotite. Amounts up to 25 percent by volume of interstitial quartz, albite, ankerite, calcite and pyrite are present. Secondary sphene that developed during greenschist facies metamorphism is found in most of the sandstones examined. The framework grains are predominantly quartz and feldspars (microcline, albite, perthite and oligoclase) with small amounts of rock fragments and micas. The detrital microcline is albitized to a variable extent. The stratigraphy,

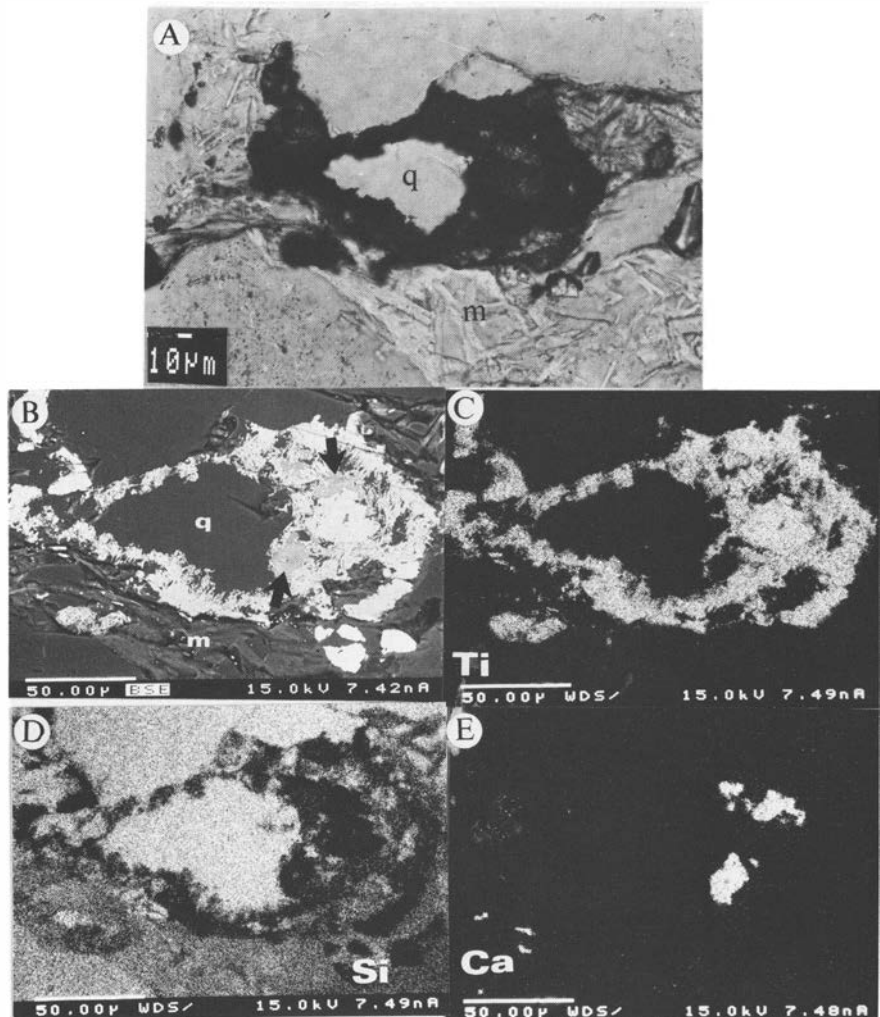


Fig. 3. A pseudomorph of quartz, anatase and calcite.

(A) Photomicrograph (+ nic.) showing the presence of a coarse, single quartz crystal (q); dark areas are mainly Ti-oxides.

(B) BSE image of the pseudomorph in micrograph 3A showing the presence of quartz (q and relatively dark grey areas), Ti-oxides (light) and calcite (arrows and light grey areas); m = phyllosilicate and quartz matrix. (C-E) X-ray scanning micrographs of Ti, Si and Ca, respectively of the pseudomorph in micrograph 3A.

sedimentology and tectonics of the Brøttum Formation have been described in detail by Englund (1972, 1973 a,b) and Nystuen (1982).

Microprobe analyses and backscattered electron imaging (BSE) were performed on polished carbon-coated thin sections using a CAMECA Camebax BX50 microprobe. Standards used for the analyses were natural sphene and ankerite. X-ray diffraction analysis (using Ni-filtered $\text{CuK}\alpha$ radiation) of samples containing appreciable amounts of

titanium minerals (obtained by magnetic separation and heavy liquid methods) were performed. Due to the fine grained nature of the Ti-oxides, the identification of different polymorphs was achieved using a combination of XRD data, optical properties and crystal habit. Small chips from four samples were coated with a thin layer of gold and examined by a JEOL JSM 840 scanning electron microscope (SEM) equipped with an energy dispersive X-ray analyser (EDS). The equilibrium diagram presented

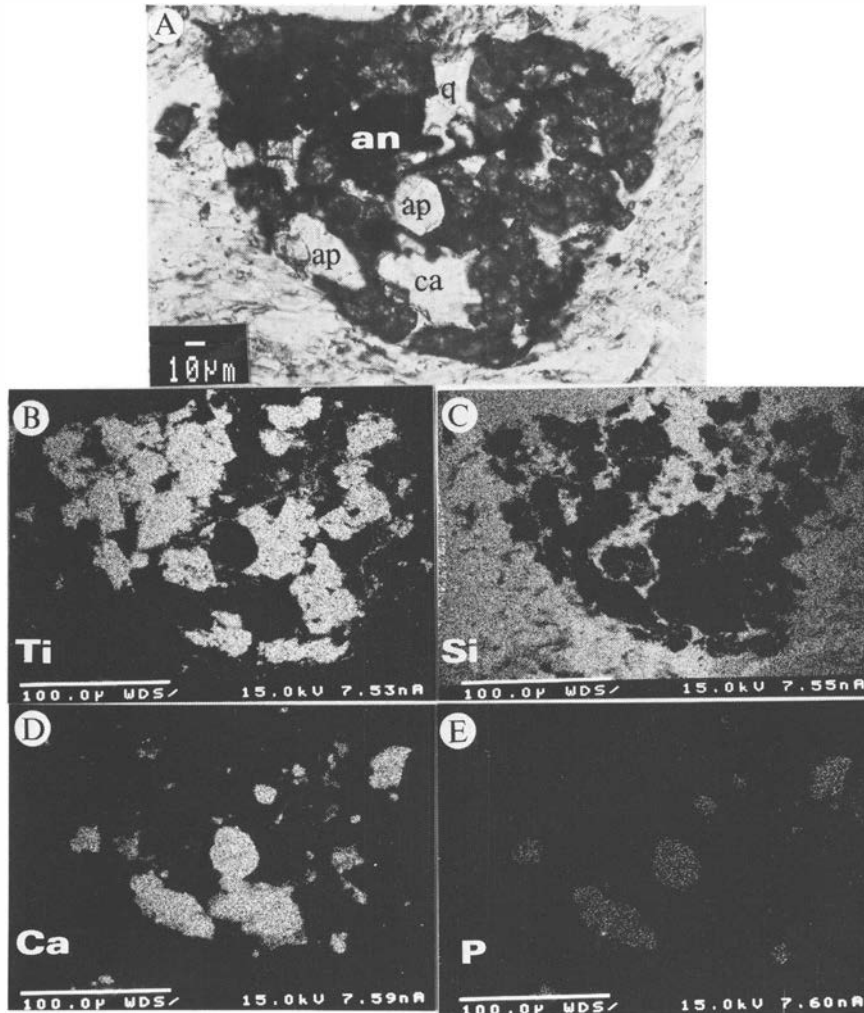


Fig. 4. (A) Photomicrograph (polarized light) of a pseudomorph of anatase (an and dark areas), quartz (q), calcite (ca) and apatite (ap). (B–E) X-ray scanning micrographs of Ti, Si, Ca and P of the pseudomorph in micrographs 4A and 4B.

in this paper was calculated using the computer program SUPCRT described by Helgeson et al. (1978).

Textural and mineralogical characteristics of altered sphene

Detrital sphene is generally absent in the sandstones studied, though sphene is a common accessory mineral in the granitic source rocks (cf. Englund 1972) and pebbles which are embedded in the Brøttum sandstones. Instead, pseudomorphs after sphene are present, consisting of Ti-oxides as well as calcite

and/or quartz. The Ti-oxides are mostly acute bipyramidal crystals of anatase and, in a few cases, prismatic and needle-like rutile. The textural relationships and volumetric proportion among Ti-oxides, calcite and quartz vary from one pseudomorph to another. In most cases, however, the overall shape of the pseudomorphs is apparently defined by Ti-oxide crystals.

Calcite and quartz are usually concentrated in the central parts of the pseudomorphs and are enveloped by few, relatively large (up to 100 μm) crystals of anatase or by a layer made of fine anatase crystals. However, intimate intergrowths between ana-

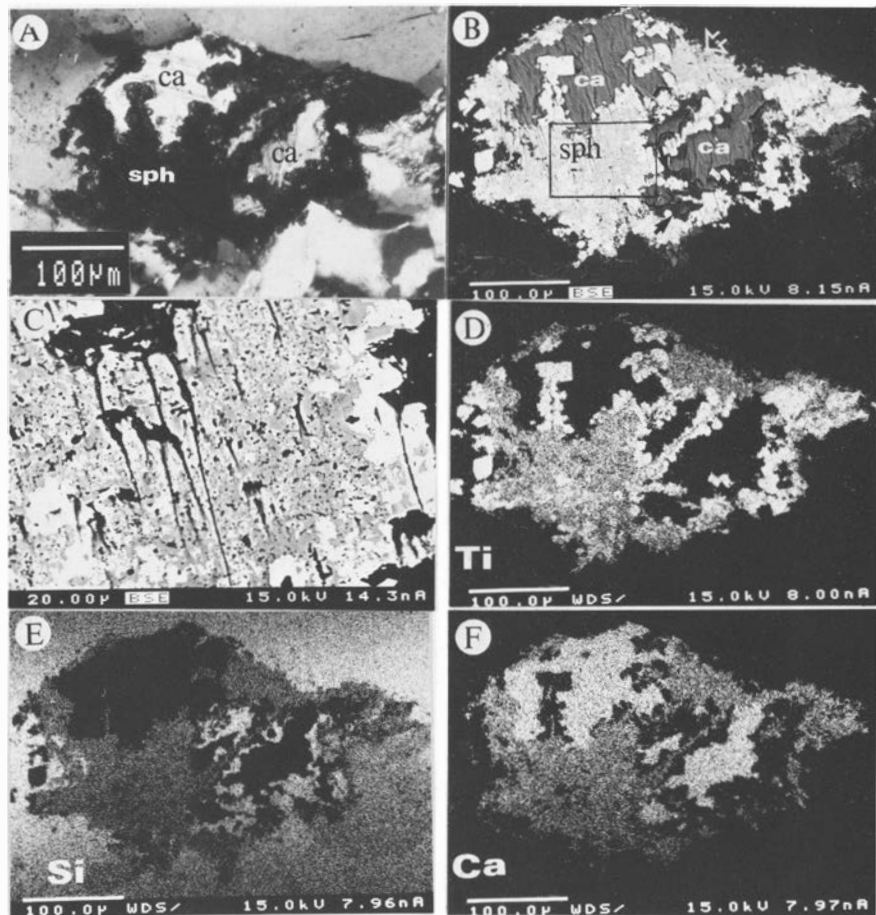


Fig. 5. (A) Photomicrograph (+ nic.) of a detrital sphene (sph) which is partly altered into calcite (ca), Ti-oxides and quartz; greyish grains around the pseudomorph are mainly detrital quartz. (B) BSE image of micrograph 5A showing the presence of very fine-crystalline Ti-oxides (light) within and around sphene (sph, open arrows and very light areas), calcite (ca; light grey) and quartz (black solid arrows and dark grey areas). (C) Enlarged view of outlined areas in micrograph 5B showing Ti-oxides (light) heavily clouded by relict detrital sphene (light grey). (D-F) X-ray scanning micrographs of Ti, Si and Ca, respectively of the pseudomorph in micrograph 5A and 5B.

tase and calcite or quartz were also observed (Fig. 2A-E); calcite might occur as few tiny inclusions (Fig. 2F). In such cases, the anatase crystals are arranged in arrays that appear as microveinlets that cut more or less irregularly through, and partly outline, the pseudomorphs (Figs. 2A-C). The quartz in this and most other pseudomorphs appears as several intergrown crystals (<30 μm in size). Lenticular and occasionally equant quartz crystals occur along the outer margins of the pseudomorphs (cf. Corlett & McIlreath 1974). Pseudomorphs in which a single but relatively large (up to 100 μm) quartz crystal is enveloped by numerous tiny crys-

tals of, apparently, needle-like rutile and intergrown anatase crystals were also observed (Fig. 3). Intimately intergrown fine crystalline quartz, Ti-oxides and, in some instances, calcite were found (Figs. 3B-E). Rarely, there are pseudomorphs in which quartz occurs almost completely along the outer boundary enveloping Ti-oxides and calcite.

In addition to the above mentioned minerals characteristic of sphene pseudomorphs, there are occasionally variable amounts of apatite (Fig. 4). Sometimes, the amounts of apatite exceed that of calcite (e.g. Figs. 4D, E). This apatite is apparently detrital in origin as it also occurs as inclusions in

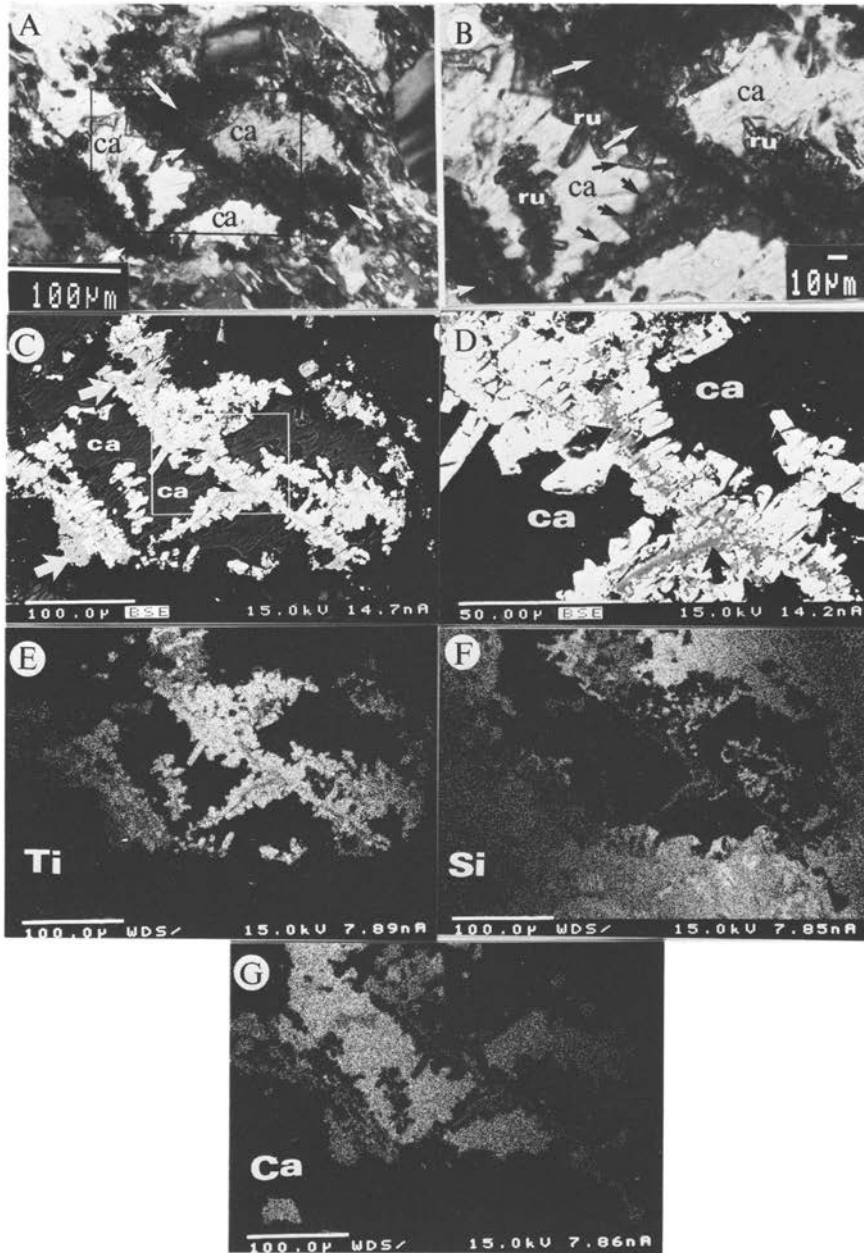


Fig. 6. (A) Photomicrograph (+ nic.) of a detrital sphene which has been pervasively altered into, mainly, Ti-oxides (dark) and calcite (ca); arrows show relict sphene. (B) Enlarged view of outlined area in micrograph 6A showing presence of rutile (ru) and anatase (dark arrows) crystals which are arranged as "microveinlets" which enclose relict sphene (white arrows and very dark areas). (C) BSE image of micrograph 6A; arrows show relict sphene enclosed by the Ti-oxide "microveinlets" (light) and along the peripheries of the pseudomorph (lower left); ca and greyish areas are calcite. (D) Enlarged BSE image of area outlined in micrograph 6C showing detailed relationship between the Ti-oxides (light) and relict sphene (light grey); ca and dark grey areas are calcite. (E-G) X-ray scanning micrographs of Ti, Si and Ca, respectively of the pseudomorph in micrograph 6A and 6B.

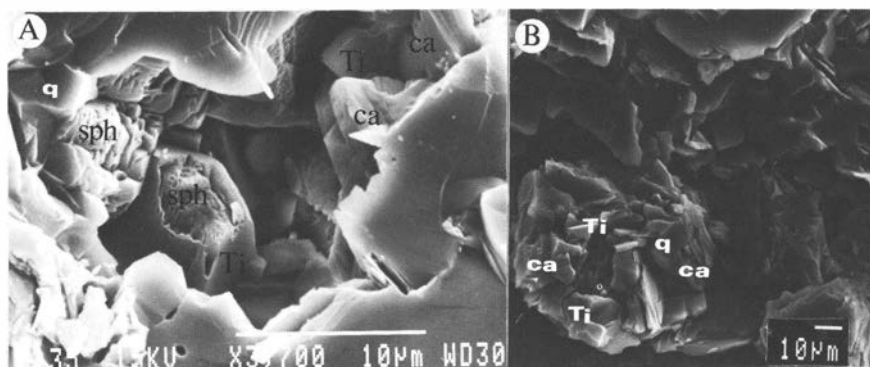


Fig. 7. (A) SEM micrograph of sphene grain (sph) which is etched and substantially replaced by Ti-oxides (Ti), quartz (q) and calcite (ca). (B) SEM micrograph of a pseudomorph composed of fine-crystalline Ti-oxides (Ti), quartz (q) and calcite (ca).

some of the sphene crystals in the granitic source rocks. In a few pseudomorphs, authigenic pyrite crystals were observed. Corlett & McIlreath (1974) have reported iron minerals (hematite or limonite) adjacent to sphene pseudomorphs in Ordovician limestones from Canada.

Few pseudomorphs contain variable amounts of relict detrital sphene which coexist with Ti-oxides, calcite and, often, small amounts of quartz (Fig. 5). The sphene is usually pervasively replaced by tiny Ti-oxide inclusions (Figs. 5B–D); Ti-oxides occur also as somewhat larger crystals along the boundaries of relict sphene (Figs. 5B, D). In such Ti-oxide crystals there are tiny inclusions of relict detrital sphene (Fig. 5C). Quartz usually occurs as thin layers between calcite and Ti-oxides domains and/or as fine crystals intergrown with the Ti-oxides (e.g. Figs. 5B, E). At a more advanced stage of alteration, relict sphene (Fig. 6) appears as minute inclusions and thin layers embedded in numerous crystals of rutile and/or anatase (Figs. 6A–D). Small amounts of relict sphene (severely replaced by Ti-oxides) may be found along the peripheries of the pseudomorphs (Figs. 6A, C, E–G). Upon complete alteration of sphene grains in figures 5 and 6, one would perhaps expect the development of Ti-oxide microveinlets similar to those shown in figure 2.

SEM examination revealed that the relict sphene is etched and usually coated with a thin (<2 μm) layer of Ti-oxide characterized by a smooth surface texture (Fig. 7A). Discrete euhedral crystals of anatase, calcite and quartz replace the sphene in figure 7. Rounded aggregates composed of intergrown Ti-oxides, calcite and quartz were also observed (Fig. 7B).

Secondary sphene developed during greenschist metamorphism commonly occurs as relatively fine crystals (5–50 μm in size) which are usually ovoidal in shape and occupy interstitial space or are embedded in altered detrital biotite and Fe-Ti oxides (Fig. 8). Secondary sphene was also occasionally observed to occur as rounded aggregates made of numerous ovoidal crystals embedded in interstitial matrix. The overall shape of these sphene-crystal aggregates resembles that of the pseudomorphs described above. Commonly, one or more types of secondary sphene and the Ti-oxide + calcite + quartz pseudomorphs coexist on the scale of thin section. However, with increasing grade of metamorphism there is a tendency for the rounded

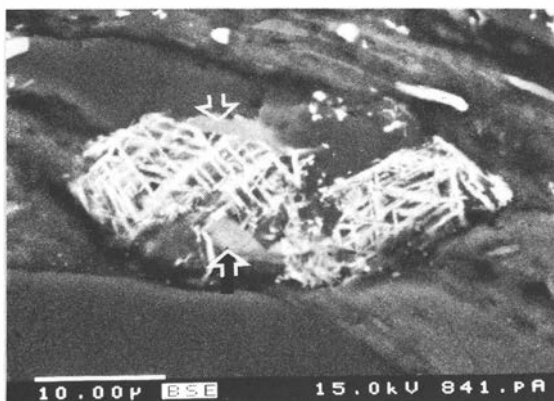


Fig. 8. BSE image of an ilmeno-magnetite which is replaced by Ti-oxides (light; that inherited the trellis-like texture by replacing ilmenite lamellae occurring along (111) planes of host magnetite) and metamorphic sphene (arrows and greyish areas between the Ti-oxide lamellae).

aggregates of sphene crystals to increase in abundance, whereas the pseudomorphs described above decrease substantially. Additional textural characteristics and chemistry of authigenic sphene are presented elsewhere (AlDahan & Morad 1986).

Mineral chemistry of sphene pseudomorphs

Microprobe analyses of calcite in the pseudomorphs described above reveal a slightly manganiferous composition (amounts of rhodochrosite solid-solution are 2 to 4 mole percent; Table 1). There are smaller amounts of siderite (0.1 to 1.5 mole percent) and magnesite (0.1 to 0.8 mole percent) solid-solutions. Unfortunately, no chemical analyses were provided for calcite found in similar sphene pseudomorphs by Corlett & McIlreath (1974) and Morad & AlDahan (1985), so that no comparison can be made. Corlett and McIlreath have, however, mentioned that the calcite they observed was slightly iron-bearing. The anatase and rutile analysed have revealed an almost pure TiO₂ composition with minor amounts of, mainly, iron (<0.4 weight percent FeO).

Microprobe analyses were performed on relict sphene in the pseudomorphs and on sphene which occurs in pebbles (i.e. source rocks) in Brøttum sandstones (Table 2). Both types of sphene show

Table 1. Representative microprobe analyses of calcite in the pseudomorphs of Ti-oxides + calcite + quartz.

	1	2	3	4	5	6
FeCO ₃	0.62	1.53	0.05	0.21	0.57	0.45
MnCO ₃	4.11	3.00	1.89	3.36	3.80	3.14
MgCO ₃	0.78	0.65	0.08	0.58	0.61	0.65
CaCO ₃	94.50	94.82	97.98	95.58	95.02	95.76

appreciable substitution of Al and Fe³⁺ for Ti which is coupled with substitution of OH⁻ and F⁻ for O²⁻, as follows: (Al, Fe³⁺) + (OH,F)⁻ = Ti⁴⁺ + O²⁻ (cf. Ekström 1972; Higgins & Ribbe 1976). The amounts of Al are greater than of Fe³⁺ in all the sphenes analysed (cf. Higgins & Ribbe 1976; AlDahan & Morad 1986; Yau et al. 1987). Al occupies, on average, 10 percent of the octahedral sites while Fe³⁺ occupies 2 percent of these sites. In some of the sphenes, there is a relatively significant substitution of Mg²⁺ for Ca²⁺. It should, however, be pointed out that some authors have concluded that small amounts of Fe³⁺ might replace tetrahedral Si too (e.g., Muir et al. 1984) and that Fe²⁺ might be present in the Ca-dominated sites (e.g. Coombs et al. 1976). MnO, Na₂O and K₂O are all present in amounts that fall within the analytical error of the microprobe, thus were not included in the

Table 2. Representative microprobe analyses of relict sphene (1-5) and of sphene in the granitic pebbles (6-9). Number of ions is calculated on the basis of 12 cations.

	1	2	3	4	5	6	7	8	9
SiO ₂	30.29	32.17	31.36	30.60	31.39	29.21	31.20	31.39	31.82
TiO ₂	33.28	32.77	30.86	35.79	31.60	37.89	30.88	32.10	34.29
Al ₂ O ₃	3.35	1.83	3.93	1.26	3.00	1.34	3.24	2.91	1.76
Fe ₂ O ₃ *	0.13	0.15	1.00	0.28	1.70	0.58	1.87	0.59	0.15
MnO	0.05	0.04	0.00	0.03	0.02	0.00	0.00	0.00	0.00
MgO	0.45	0.03	0.49	0.02	0.02	0.02	0.59	0.02	0.00
CaO	27.50	27.54	27.56	27.69	27.91	25.57	26.71	28.01	28.52
Na ₂ O	0.11	0.11	0.08	0.02	0.03	0.00	0.03	0.03	0.00
K ₂ O	0.08	0.07	0.04	0.08	0.04	0.02	0.02	0.03	0.02
F	1.23	0.72	1.01	0.55	1.05	0.64	0.98	1.11	0.37
	96.47	95.43	96.33	96.32	96.76	95.27	95.52	96.18	96.92
O≡F	0.51	0.30	0.42	0.22	0.44	0.26	0.41	0.46	0.15
Total	95.96	95.13	95.91	96.10	96.32	95.01	95.19	95.72	96.77
Si	4.06	4.32	4.17	4.13	4.19	4.02	4.20	4.21	4.22
Ti	3.36	3.40	3.09	3.63	3.17	3.94	3.12	3.24	3.43
Al	0.53	0.29	0.61	0.20	0.47	0.22	0.51	0.46	0.28
Fe ³⁺	0.02	0.02	0.10	0.03	0.17	0.06	0.19	0.06	0.02
Ca	3.95	3.97	3.93	4.01	3.99	3.77	3.86	4.03	4.06
Mg	0.09	0.00	0.10	0.00	0.00	0.00	0.12	0.00	0.00

* Fe₂O₃ represents total iron

formula calculation. A microprobe survey for ZrO_2 , Nb_2O_5 , La_2O_3 , Ta_2O_5 , Ce_2O_3 and Nd_2O_3 indicates that these elements are below the detection limit of the microprobe.

Discussion

Mineralogical composition (Ti-oxides, quartz and/or calcite) and overall shape of the pseudomorphs described above are reliable criteria which indicate formation upon decomposition of detrital sphene (cf. Pough 1934; Corlett & McIlreath 1974; Morad & AlDahan 1986). The presence, in the granitic source rocks, of sphene with a size and chemical composition which are comparable to size of the pseudomorphs and the chemistry of relict sphene, respectively, further supports this conclusion. Criteria which indicate an in-situ origin of the pseudomorphs include: 1) the commonly euhedral shape of minerals and the fragile texture of the pseudomorphs (these textures are usually destroyed during transportation and reworking of sediments); 2) the generally unaltered nature of sphene in the source rocks. The microprobe analyses of calcite in slightly altered sphene in the source rock revealed a pure $CaCO_3$ composition whereas calcite in the pseudomorphs is Mn-richer (Table 1); 3) the presence of apatite in the Ti-oxide + calcite + quartz pseudomorphs and in sphene of the granitic pebbles.

The presence of metamorphic sphene and Ti-oxide + calcite + quartz pseudomorphs on thin section scale, particularly in the lower-grade sandstones, indicates that decomposition of detrital sphene occurred during diagenesis and before that T-P- X_{CO_2} conditions (prevailing during the greenschist metamorphism) had resulted in stabilization of sphene. At the low temperature conditions of diagenesis, decomposition of sphene occurs at low X_{CO_2} (Fig. 9). Although the exact diagenetic stage at which decomposition of detrital sphene occurred is difficult to evaluate, the manganiferous composition of the calcite suggests early diagenesis just below the sediment-water interface in the deep-marine depositional environment of the Brøttum Formation (see, e.g., Strakhov 1965; Ostwald 1987). Furthermore, metamorphic sphene did not preferentially form at the expense of Ti-oxides + quartz + calcite of the pseudomorphs. The latter means that decomposition of sphene might be irreversible, at least up to deep-burial diagenesis to "lowermost" greenschist facies (chlorite zone) of metamorphism due to kinetic reasons. The latter could, however, be partly related to the manganiferous composition of the calcite in the pseudomorphs.

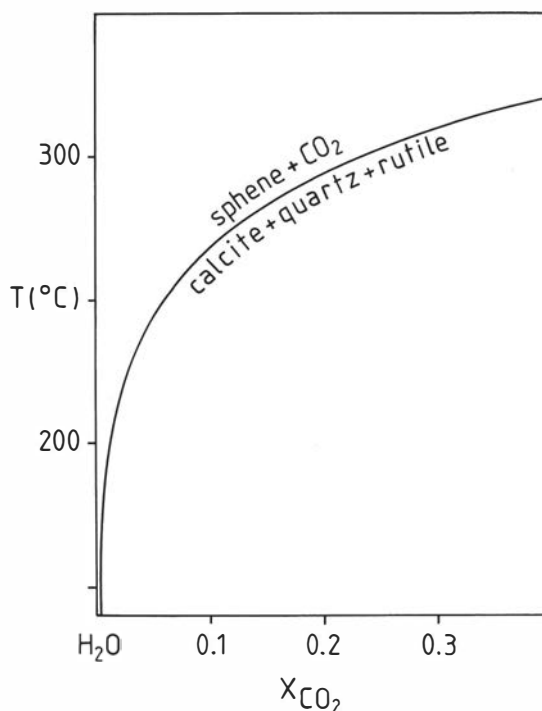
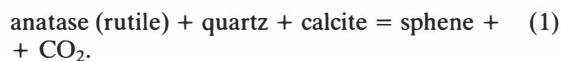


Fig. 9. T- X_{CO_2} phase equilibrium at $P_{H_2O} = 0.1Kb$ for ideal mixing of H_2O and CO_2 for rutile + calcite + quartz = sphene + CO_2 (after Yau et al. 1987).

The occurrence of metamorphic sphene in such sandstones as pore-fillings and within altered biotite and Fe-Ti oxides suggests that it was formed by crystallization from pore fluids (cf. Yau et al. 1987) and by decomposition of detrital biotite and Fe-Ti oxides. The occurrence of rounded aggregates of sphene crystals, particularly with increasing grade of metamorphism, suggests formation at expense of the Ti-oxide + calcite + quartz pseudomorphs. This is supported by the concomitant decrease in abundance of these pseudomorphs.

The petrographic observations described above suggest that phase equilibrium conditions during greenschist metamorphism were principally controlled by X_{CO_2} of the pore fluids (e.g. Schulling & Vink 1967; Hunt & Kerrick 1977; Fig. 9), according to the following reaction:



Thus, sphene in greenschist facies (temperature of 250°C to 350°C; Morad 1986) is stable at a higher X_{CO_2} in the pore fluids when compared to diage-

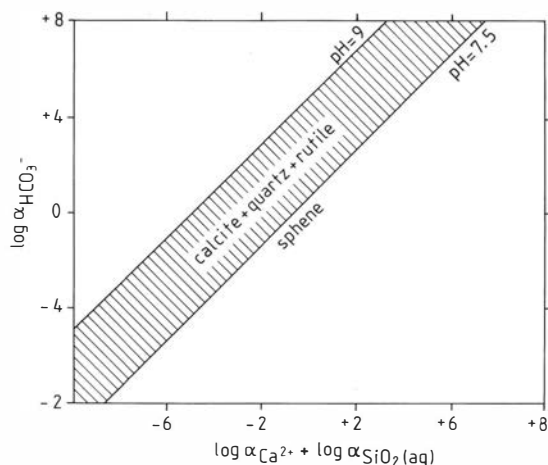
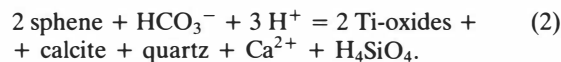


Fig. 10. Equilibrium diagrams (at 25°C and 1 atm.) of reaction 2. Shaded area shows the likely stability field of rutile + calcite + quartz.

netic conditions (Fig. 9). Furthermore, the presence (beside Ti-oxides) of either predominantly calcite (Fig. 6) or quartz (Fig. 2) in the diagenetic sphene pseudomorphs indicates the influence of pH in the pore fluids (cf. Corlett & McIlreath 1974; Morad & AlDahan 1985). At a pH higher than 9.0, silica dissolves readily, whereas precipitation of calcite is enhanced. Conversely, solubility of calcite increases and silica precipitation is enhanced at pH lower than 7.5. Accordingly, pseudomorphs composed of Ti-oxides, quartz and calcite (Fig. 3) indicate that decomposition of sphene has occurred at a pH of about 7.5 to 9.0 (cf. Blatt et al. 1980). Thus, in diagenetic environments reaction 1 is expected to be closely related to pH (α_{H^+}), X_{CO_2} ($\alpha_{\text{HCO}_3^-}$), $\alpha_{\text{Ca}^{2+}}$ and $\alpha_{\text{H}_4\text{SiO}_4}$ as tentatively expressed by the following reaction and the equilibrium diagram in figure 10:



Conclusions

1) Through diagenetic decomposition, detrital sphene can be substantially to completely replaced by pseudomorphs composed of Ti-oxides (anatase and, less commonly, rutile) as well as calcite and/or quartz. The decomposition and its products are greatly influenced by activities of HCO_3^- , H^+ , Ca^{2+} and H_4SiO_4 in the pore solutions.

2) Petrographic observations carried out show that the right side of the phase equilibrium reaction: Ti-oxide + calcite + quartz = sphene + CO_2 is favoured with relative increase in grade of greenschist-facies metamorphism. During deep-burial diagenesis to lowermost greenschist facies, sphene is preferably formed by crystallization from pore fluids and by decomposition of detrital biotite and Fe-Ti oxides.

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