*The Canadian Mineralogist*
Vol. 34, pp. 1223-1232 (1996)

# CATHODOLUMINESCENCE INVESTIGATIONS AND TRACE-ELEMENT ANALYSIS OF QUARTZ BY MICRO-PIXE: IMPLICATIONS FOR DIAGENETIC AND PROVENANCE STUDIES IN SANDSTONE

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## ABSTRACT

Hot-cathodoluminescence (CL) microscopy and high-resolution trace-element analyses by Particle Induced X-ray Emission (micro-PIXE) using the proton microprobe have been applied to samples of quartz arenite in order to obtain information about their diagenetic environment and the provenance of quartz detritus. The occurrence of an intensely zoned orange-brown cement generation within quartz overgrowths in quartzitic lenses from the Fontainebleau Sand (Oligocene, Paris Basin) coincides with increased Fe concentrations of up to 192 ppm. In contrast, the Fe content of a nonluminescing generation within the same overgrowths is significantly lower. This finding suggests that the CL is either activated by the Fe itself or caused by defects induced by the incorporation of Fe into the structure. Detrital grains of quartz from sandstone samples of different ages and locations (Wiehengebirgsquarzit, Upper Jurassic, northwestern Germany; Fontainebleau Sand, Oligocene, Paris Basin) yield a good correlation between CL color and Fe and Ti concentrations, with Fe (up to 455 ppm) being more abundant in red-brown-luminescing grains and Ti (up to 298 ppm) confined to grains with blue-violet luminescence. Ti is universally present in quartz from plutonic and extrusive igneous rocks, but rarely observed in quartz from metamorphic rocks. This supports the general contention that the blue-violet-luminescing quartz was formed under higher temperatures than the quartz with brown luminescence, an observation important for studies of sandstone provenance. Concerning the mechanisms of CL activation, these results do not unequivocally prove that the observed colors are activated by the elements sought. Despite the advantages of the microanalytical technique, the observed trace-element contents may still reflect submicroscopic inclusions rather than element incorporation into the structure.

*Keywords:* cathodoluminescence microscopy, proton microprobe, micro-PIXE, trace elements, quartz arenite, authigenic quartz, detrital quartz, diagenesis, provenance studies.

## SOMMAIRE

Nous nous sommes servis de cathodoluminescence à chaud, observée avec un microscope, et de données ponctuelles de teneurs en éléments traces, obtenues avec une microsonde protonique (technique micro-PIXE), pour étudier des échantillons d'arénite quartzifère, afin d'en savoir plus long à propos du milieu de diagenèse et la provenance des détritus. La présence d'une génération de ciment fortement zoné, à luminescence orange-brun, dans les surcroissances de quartz dans les lentilles de quartzite du grès de Fontainebleau (bassin de Paris) coïncide avec une concentration accrue en Fe, jusqu'à 192 ppm.

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Par contre, la teneur en Fe des domaines sans luminescence dans les mêmes surcroissances est beaucoup plus faible. Cette observation fait penser que la cathodoluminescence est soit activée par la présence de Fe dans le réseau, soit le résultat de défauts cristallins dus à l'incorporation du Fe dans la structure. Des grains de quartz détritiques provenant d'échantillons de grès d'âge et d'endroits variés (Wiehengebirgsquarzit, jurassique supérieur, nord-ouest de l'Allemagne; grès de Fontainebleau, oligocène, bassin de Paris) montrent une bonne corrélation entre couleur observée par cathodoluminescence et concentrations de Fe et de Ti. La teneur en Fe, jusqu'à 455 ppm, est plus élevée dans les grains à luminescence rouge-brun, tandis que le Ti, jusqu'à 298 ppm, est limité aux grains à luminescence bleu-violette. Le Ti est ubiquiste dans le quartz provenant de roches ignées, soit plutoniques ou extrusives, mais rarement observé dans le quartz métamorphique. Ces observations étayent l'hypothèse voulant que le quartz à luminescence bleu-violette ait cristallisé à une température plus élevée que la quartz à luminescence brune, qui s'avère importante dans les études de provenance des grès. Pour ce qui est des mécanismes d'activation de la cathodoluminescence, nos résultats ne montrent pas de façon non équivoque que les couleurs observées sont activées par les éléments traces dont nous avons mesuré la concentration. Malgré les avantages de la technique micro-analytique, les teneurs en élements traces pourraient résulter d'inclusions submicroscopiques plutôt que l'incorporation de ces élements dans le réseau.

(Traduit par la Rédaction)

*Mots-clés:* cathodoluminesce avec microscopie, microsonde protonique, micro-PIXE, éléments traces, arénite quartzifère, quartz authigène, quartz détritique, diagenèse, provenance.

## INTRODUCTION

Syntactic overgrowths of quartz in quartz-rich sandstone (quartz arenite) typically show two basic patterns of cathodoluminescence (CL): (1) relatively stable brown, red-brown or dark blue CL (Zinkernagel 1978, Houseknecht 1987, Morad *et al.* 1991) and (2) blue, green, yellow or red colors that are unstable under electron bombardment (Burley *et al.* 1989, Ramseyer & Mullis 1990). The first type of CL is believed to have been generated by burial diagenetic conditions, with temperatures resulting from the conductive geothermal gradient (*e.g.*, Bruhn & Richter 1993). The second type of CL has mostly been interpreted as reflecting precipitation from hot basinal brines or possibly from hydrothermal solutions (*e.g.*, Zinkernagel 1978, Neuser *et al.* 1989, Burley *et al.* 1989, Perny *et al.* 1992). The previously frequently quoted non-luminescing quartz, interpreted as characteristic of the diagenetic variety (*e.g.*, Zinkernagel 1978), seems to be a rare phenomenon, particularly when observed with a "hot-CL" device (*e.g.*, Ramseyer *et al.* 1988, Burley *et al.* 1989, Walker & Burley 1991, Stroink 1993, Bruhn & Richter 1993). Detrital quartz grains in sandstones typically luminesce in various shades of blue, violet, brown or red (*e.g.*, Zinkernagel 1978, Marshall 1988, Neuser *et al.* 1989).

When coupled with transmitted light microscopy; a CL microscope can commonly provide additional information that can be utilized to confront three fundamental issues of sandstone petrology: (a) provenance of detrital quartz grains (*e.g.*, Zinkernagel 1978, Füchtbauer *et al.* 1982, Massonne 1984, Owen 1991), (b) quantification of compaction and cementation processes in sandstones (*e.g.*, Sippel 1968, Sibley & Blatt 1976, Houseknecht 1984, 1987, 1991), and (c) chronological and geochemical reconstruction of quartz cementation (*e.g.*, Blatt 1979, Fisher & Land 1986, Suchecki & Bloch 1988, Burley *et al.* 1989, Walker & Burley 1991, Bruhn & Richter 1993).

Despite considerable benefits of the phenomenological investigation of CL colors in quartz, the question of what produces them is still far from being resolved. This is due partly to the extreme chemical purity of quartz and partly to the fact that, apart from incorporation of trace elements (*cf.* Richter & Zinkernagel 1975, Sprunt 1981, Ramseyer *et al.* 1988, Ramseyer & Mullis 1990, Perny *et al.* 1992), quartz CL is strongly influenced by structural defects (*cf.* Zinkernagel 1978, Ramseyer *et al.* 1988, Owen 1988, Meunier *et al.* 1990). Clearly, only those elements that can be incorporated into the quartz structure can be considered to influence CL, either as CL activators or as causes of structural defects. Yet, judging from bulk analytical techniques, even these elements tend to occur in fluid or mineral inclusions rather than in the quartz structure (*cf.* Deer *et al.* 1966, Bambauer 1961, Siebers 1986), and they may even be contaminants derived from sample preparation.

Until now, only a few elements have been postulated to activate CL in quartz. These are Ti and Fe (Sprunt 1981), Al (Grant & White 1978, Perny *et al.* 1992), $H^+$ and $Li^+$ (Matter & Ramseyer 1985, Perny *et al.* 1992), Mn (Richter & Zinkernagel 1975, Dudley 1976) $OH^-$ and $H_2O$ (Behr 1989), and Ga (Dudley *et al.* 1976).

Trace-element concentrations in quartz have only seldom been used for tracing the conditions of mineral formation in sedimentological samples. The examples are the provenance studies from bulk-mineral analyses (Sprunt 1981, Götze & Lewis 1994) and the studies of trace elements in diagenetic and hydrothermal quartz (Siebers 1986, Ramseyer & Mullis 1990, Gerler 1990, Perny *et al.* 1992). The latter group of authors, utilizing a microanalytical tool (Secondary Ion Mass Spectrometry – SIMS), found evidence for elevated $Al^{3+}$ contents in short-lived blue-luminescing zones in crystals of hydrothermal quartz.

The above discussion clearly documents a need for a microsampling technique that could advance our understanding of the nature of CL activation in quartz and its utility for diagenetic and provenance studies. Micro-PIXE represents one such tool. The main purpose of this paper is to present two case studies where a combination of CL microscopy with PIXE microanalysis of diagenetic and detrital quartz enabled advances in sedimentological interpretations.

## SAMPLES STUDIED

In order to test these techniques, two localities with quartz arenite showing abundant diagenetic and detrital quartz have been selected; they are described below.

### *Fontainebleau Sand*

The Fontainebleau Sand is a 50- to 60-m thick, fine-grained, well-sorted sand of early Oligocene age (Alimen 1936). In the area south of Paris, it is mostly covered by the late Oligocene and early Miocene Etampes and Beauce limestone, and its outcrops are restricted to clefts at the flanks and within the Beauce plateau. Quartzite lenses, of 2 to 8 m thickness, have been formed during the Pleistocene (<400,000 a) by a silicification process that was controlled by a fluctuating groundwater table during geomorphological evolution (Thiry & Bertrand-Ayrault 1988). Quartz cementation appears to have taken place very rapidly, with approximately 30,000 years required for cementation of a single lens of quartzite (Thiry & Bertrand-Ayrault 1988, Thiry *et al.* 1988).

The three samples investigated for their CL characteristics were collected from the quarry "La Muette" at Elancour, west of Trappes. They are relatively pure and well-sorted quartz arenite, with a framework composition of 98 to 100% total quartz and porosities of 10 to 21%. The samples of arenite are medium to fine grained. Detrital quartz grains either have abundant mineral or fluid inclusions or are virtually inclusion-free, as are the quartz overgrowths. CL of detrital quartz is red-brown (29 to 35% of the grains), brown-violet and blue-violet (59 to 65%) and red (5 to 7%). The samples have between 9 and 22% quartz cement, resulting in minus cement porosities of >30%, which is typical of low compaction. Overgrowths of authigenic quartz, with an apparent thickness of 20 to 50 μm, commonly consist of two generations with different CL features. An older, non-luminescent generation is overgrown by a younger one that, after a few seconds of electron irradiation, displays a pattern of more or less intensely orange-brown luminescing zones (Figs. 1A, B). Considering the above-cited high rate of precipitation of quartz, cementation events of a few thousand years or less may be indicated by the observed CL zonation. Trace-element concentrations for detrital and authigenic quartz in the Fontainebleau Sand were measured at several points of a single selected sample.

### *Wiehengebirgsquarzit*

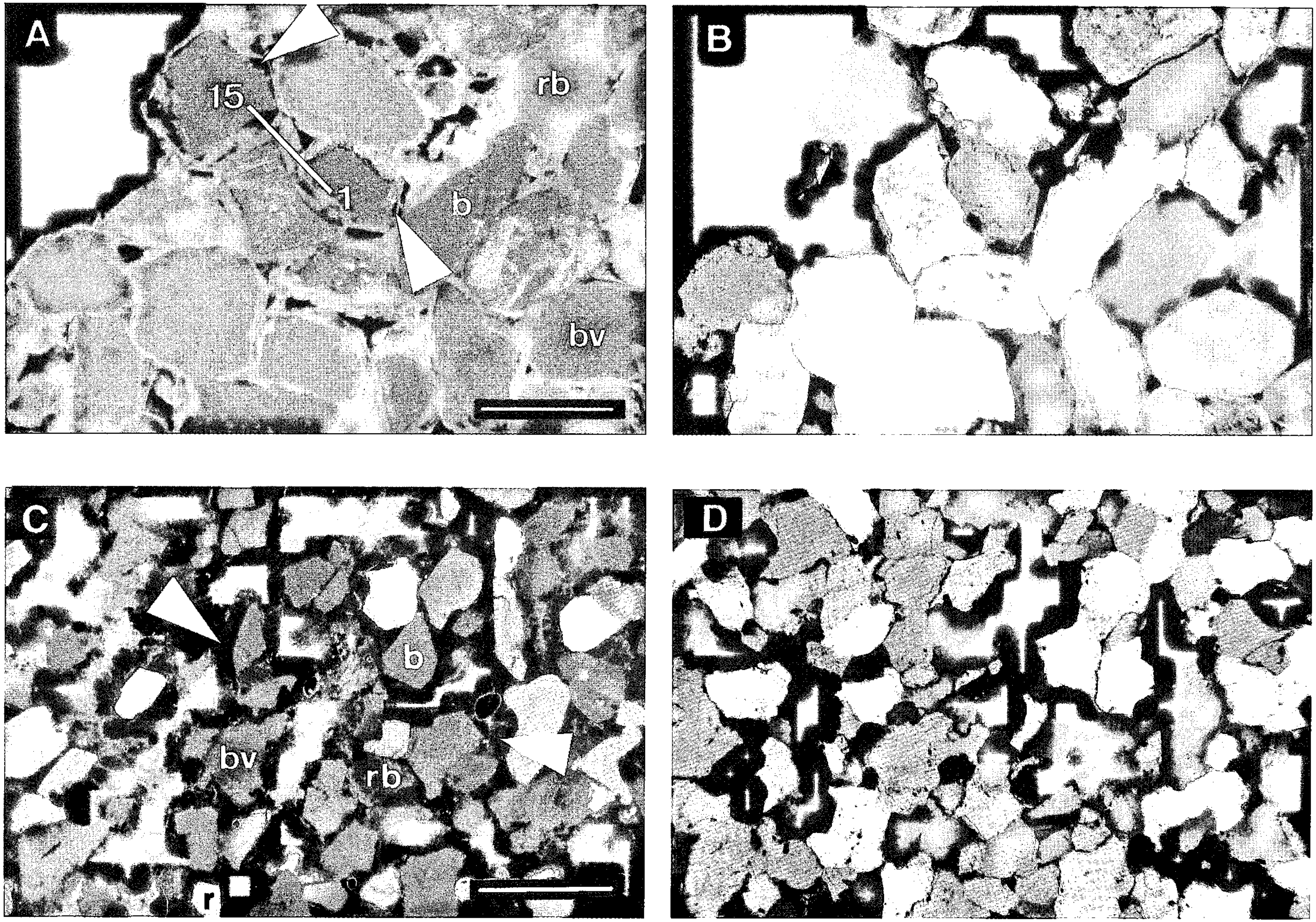
The Wiehengebirgsquarzit is a medium to fine grained, moderately to well sorted quartz arenite of littoral and fluvial origin, representing the clastic facies of the Upper Jurassic Korallenoolith Formation, deposited in the NW–SE-trending Lower Saxonian basin of northwestern Germany (Schott & Staesche 1967). The thickness in outcrops ranges between <10 and 20 m.

Thirty-one samples, taken from outcrops in the Wiehengebirge, west of the river Weser, have been investigated for their modal composition and CL behavior. Quartz (detrital grains and autigenic overgrowths) is the dominant component, accounting for 90 to 100% of the framework, with porosities of up to 18%. The CL colors of detrital quartz grains are quite variable, with 15 to 44% of the grains being red-brown, 35 to 81% brown-violet and blue-violet, and up to 13% being red-luminescing (Figs. 1C, D). The content of authigenic quartz ranges between 5 and 36%. Under CL, the overgrowths yield a succession of generations with different characteristics of luminescence (non-luminescent → red-brown → short-lived green or blue → red-brown). This succession is interpreted to mirror the evolution from burial diagenetic conditions, with temperatures caused by the conductive geothermal gradient, to enhanced convection of hydrothermal solutions expelled from the Upper Cretaceous "Bramscher Massiv" (Stadler & Teichmüller 1971), and finally to retrograde burial conditions (Bruhn 1995). Trace-element concentrations were measured on detrital quartz in one sample.

## METHODS

CL observations and trace-element analyses have been performed on polished 30-μm thin sections coated with a thin film of carbon in order to avoid charge build-up. The CL device utilized (HC1–LM, Neuser 1995) operates with a hot cathode. This results in a low threshold for CL activation, and the apparatus is therefore particularly suited to observation of the weak CL that is typical of many samples of quartz. The operating conditions were: beam energy 14 keV, beam-current density 15 μA $mm^{-2}$, and operating vacuum $<10^{-6}$ Torr. Photographs were taken using Kodak EC 400 color slide films with exposure times of ~4 minutes.

The concentrations of Ca, Ti, Fe and Pb in detrital and authigenic quartz were measured with the Bochum proton microprobe (for further details, see Meijer *et al.* 1994), using a 3 MeV proton beam generated by a dynamitron tandem accelerator. This analytical method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is virtually nondestructive, and thus enables precise control of textural relationships within the sample after analysis. The principle of PIXE is similar to that of the electron microprobe, but it has the advantage of a higher signal/noise ratio, owing to the higher mass of protons relative to electrons. This enabled detection limits at the <10 ppm level for the measured elements. Employing an electromagnetic beam-focusing system that consists of four quadrupole magnets, a lateral resolution of <10 μm was achieved. With a penetration depth of the proton beam in the 30–50 μm range, sample masses as low as 10 ng were analyzed. Owing to the high depth of penetration, care had to be taken when observing very narrow chemical zoning in minerals. Furthermore, in order to eliminate "contamination" by the underlying glass mount, the samples were mounted on silica slides. For the analysis of quartz, a Hostaphan® filter with a nominal thickness of 100 μm was mounted between the sample and the X-ray detector (energy resolution in the range of 230 eV) in order to diminish the dominant Si radiation. This resulted in shorter acquisition-times and lower detection-limits.

Measurements of trace-element concentrations were carried out as point analyses and linescans, yielding distribution profiles. The acquisition time for a single point analysis was about 10–15 minutes. Thus, with typical beam-currents of a few nA, the accumulated proton charge for each point analysis was typically in the range of 1 to 5 μC. The PIXE linescan required a longer acquisition-time of three hours. CL observations were performed prior to PIXE analyses and rechecked afterward.

The evaluation of absolute concentrations from the measured X-ray spectra was performed using the GUPIX software package (Maxwell *et al.* 1989, 1995). Utilizing a least-squares fitting procedure, this software produces a model fit to the measured spectrum (Fig. 2). The peak energy is specific for the element, and the peak area of the dominant X-ray peak of each element is proportional to its concentration. The calibration of the elemental setup, based on the solid angle of the detector and on the proton-charge integration, was established by the analysis of geological standards that are routinely utilized by the X-ray fluorescence technique. These were fused as glass discs of a 10% admixture of the NBS standard powder (AGV–1) in a Spectromelt® flux (66% dilithium tetraborate, 34% lithium tetraborate). Repeated measurements of the standard reference material AGV–1 in the course of the data acquisition ("beamtime") and their comparison with the recommended values yield an internal precision and an external accuracy of ~10% (1σ) for a number of elements (see Bruhn *et al.* 1995). Despite this permanent control of accuracy, the realistic error in the case of quartz samples is somewhat larger, in the range of 10 to 20% (1σ). This is a consequence of the almost complete elimination of the Si X-ray peaks by the applied filter, resulting in elimination of the quantitative control of Si values in the quartz samples.

## RESULTS AND DISCUSSION

### *Diagenetic quartz*

In the Fontainebleau Sand, a PIXE linescan across detrital quartz grains and their overgrowths of authigenic quartz (Figs. 1, 3) shows elevated Fe concentrations in the orange-brown-luminescing generation. In order to further corroborate this observation, subsequent PIXE point measurements have been located in microscopically inclusion-free areas within the overgrowths (Fig. 4). The Fe content of the non-luminescing generation ranges between 12 and 59 ppm, whereas significantly higher values, of 98 to 192 ppm, have been observed within the generations with the orange-brown luminescence. This agrees well with other observations and postulated correlations between (red-)brown CL and incorporation of iron (particularly $Fe^{3+}$) into the quartz structure (*e.g.*, Sprunt & Nur 1979, Sprunt 1981, Ramseyer *et al.* 1988). According to Rémond *et al.* (1992), the substitution of foreign elements for $Si^{4+}$ in the quartz structure commonly is charge-balanced by the substitution of $O^{2-}$ by $OH^-$. The same authors

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FIG. 1. A, B: Principal CL colors of detrital and diagenetic quartz within quartzitic lenses of the Fontainebleau Sand (Oligocene, Paris Basin). CL of detrital quartz: rb: red-brown, bv: brown-violet, b: blue-violet. Syntactic overgrowths on some quartz grains yield a succession of an older, non-luminescing generation (arrows), followed by a younger one with orange-brown luminescence. White line: orientation of the PIXE linescan in Figure 3. A: CL, B: crossed nicols; scale bar equals 500 μm. C, D: Principal CL colors of detrital and diagenetic quartz within the Wiehengebirgsquarzit (Upper Jurassic, northwestern Germany). CL of detrital quartz: rb: red-brown, bv: brown-violet, b: blue-violet, r: red. Authigenic quartz overgrowths within this sample are characterized by a first red-brown-luminescing generation, interpreted to mirror burial diagenetic conditions, and a second generation with short-lived green CL (arrows), believed to be a response to the impregnation by hydrothermal solutions generated by the Upper Cretaceous intrusive body of the "Bramscher Massiv". C: CL, D: crossed nicols; scale bar equals 800 μm.

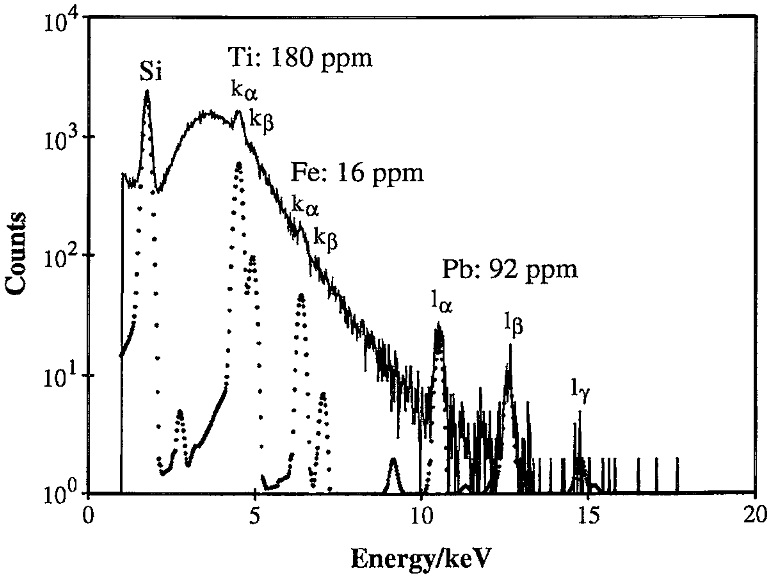

FIG. 2. Measured spectrum (solid line) and GUPIX fit (dotted line) for a sample of quartz, after background subtraction. Calculation of concentrations is based on the dominant X-ray peak of each element. Detector resolution is ~230 eV.

reported also a correlation between an emission band at approximately 650 nm (*i.e.*, in the orange-red spectral range) and the presence of $OH^-$. Likewise, the occurrence of brown luminescence that can be observed after increased electron bombardment or in radiation-damaged rims around zircon and monazite grains is commonly interpreted to be caused by damage to the quartz structure, which results in formation of unpaired, nonbonding electrons (Sprunt 1981, Ramseyer *et al.* 1988, Rémond *et al.* 1992). This effect is further magnified by the presence of substituting $Fe^{3+}$ that results in local charge-imbalance (Sprunt 1981). Consequently, assuming that submicroscopic fluid or mineral inclusions are absent, the structural incorporation of $Fe^{3+}$ represents a realistic interpretation of the shift to orange-brown CL colors in this initially nonluminescing generation of quartz.

$Fe^{3+}$ is only mobile in solutions with $pH < 3$ (Garrels & Christ 1965). Yet, considering the Pleistocene cementation of the Fontainebleau Sand (Thiry & Bertrand-Ayrault 1988), the precipitation of the authigenic quartz could have been accomplished at near-surface conditions from oxidized pore-waters that may have had low pH values owing to the presence of humic acids. In such conditions, considerable quantities of $Fe^{3+}$ may have been available for substitution. The precipitation of the nonluminescing generation, on the other hand, may be a consequence of lower concentrations of $Fe^{3+}$ in the pore waters, owing to enhanced decomposition of organic material, causing a decline in the Eh of the diagenetic milieu.

Admittedly, the above model is speculative. In order to substantiate the possible influence of climate on the observed CL patterns, a CL investigation of authigenic quartz should be carried out on a basin-wide scale. This, however, was beyond the scope of the present study.

### *Detrital quartz*

In order to obtain trace-element information complementary to the visually observed CL colors, 47 separate, homogeneously luminescing detrital grains of quartz (20 grains from the Wiehengebirgsquarzit and 27 grains from the Fontainebleau Sand) have been analyzed, with the proton beam scanned over an area of up to $50 \times 50$ $\mu m^2$. Apart from sporadic Pb and Ca concentrations, which we believe to be present in inclusions, Ti and Fe were the only elements to have been observed at concentrations above the detection limit of ~5 ppm. Ti contents reach 298 ppm, whereas Fe concentrations are up to 455 ppm. The CL colors in the present case are derived from color slides, and represent therefore the final CL features, after a few minutes of electron bombardment, rather than the initial ones. Taking into account that prolonged electron bombardment normally causes an increase in the red luminescence emission, quartz grains that

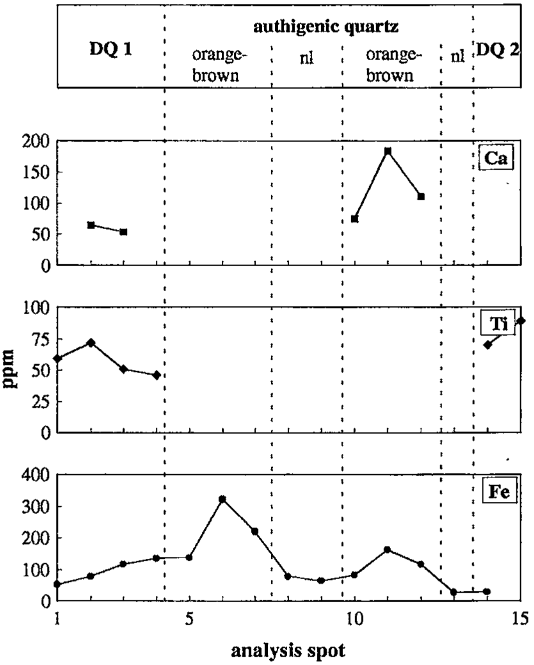

FIG. 3. PIXE linescan intersecting grains of detrital quartz and their authigenic rims (*cf.* Figs. 1A, B) in a sample from the Fontainebleau Sand (Oligocene, Paris Basin). The orange-brown-luminescing generation within the authigenic quartz is characterized by increased concentrations of Fe, if compared to the grains of detrital quartz and to the non-luminescing generations of authigenic quartz. The length of linescan is 150 μm. DQ: detrital quartz, nl: non-luminescing. Detection limits: Ca 14 ppm, Ti 7–8 ppm, Fe 2–3 ppm.

appeared to be a mixture of red-brown and blue-violet (*i.e.*, "brown-violet") are interpreted to have been initially blue-violet-luminescing. The relationships between Ti and Fe contents and the CL colors are plotted in Figure 5, where three main domains can be delineated as the result of two overlapping areas. Grains with low Ti and Fe concentrations, up to 75 and 50 ppm, respectively, have either red-brown or blue-violet CL (field A). The second field (B), with red-brown-luminescing quartz, is characterized by Ti values below 75 ppm and enhanced Fe concentrations. Field C, with blue-violet and red luminescence, has Ti concentrations in excess of 75 ppm and relatively low Fe concentrations.

A correlation between Ti and Fe contents and quartz CL has been postulated already by Sprunt & Nur (1979). Subsequently, Sprunt (1981) provided semi-quantitative confirmation using a laser microprobe. The elevated concentrations of Ti are believed to be typical of quartz derived from plutonic or eruptive rocks, rather than being of regional low-grade metamorphic origin (*e.g.*, Dennen 1964, 1966). At the same time, plutonic quartz appears to contain lower concentrations of Fe than its metamorphic and volcanic counterparts (Suttner & Leininger 1972). If so, the blue-violet-luminescing grains of quartz in our study would seem to have originated from high-grade metamorphic or plutonic source-rocks, whereas grains with red-brown luminescence were probably derived from low-grade metamorphic rocks. Given the high frequency of the two principal CL colors in the sample of sandstone studied, the chemical data indicate a mixed provenance or a significant contribution of reworked detritus. The latter alternative is further supported by the observed high compositional maturity. Yet, the generally accepted correlation of quartz CL with the type of source rocks (*e.g.*, Zinkernagel 1978, Füchtbauer *et al.* 1982, Massonne 1984, Owen 1991) is a more complex issue. For example, Neuser *et al.* (1989) demonstrated that the initial red-brown luminescence is not always confined to quartz from low-grade metamorphic environments. We propose, therefore, that provenance studies in sandstones should not be based solely on interpretation of CL colors in detrital quartz grains. The impact of such studies would increase considerably if they were combined with other methods, such as trace-element analyses (see also Götze & Lewis 1994), isotope geochemistry (*e.g.*, Elsenheimer & Valley 1993, Hemming *et al.* 1994), or microthermometry (*e.g.*, Morad *et al.* 1991, Stroink 1993).

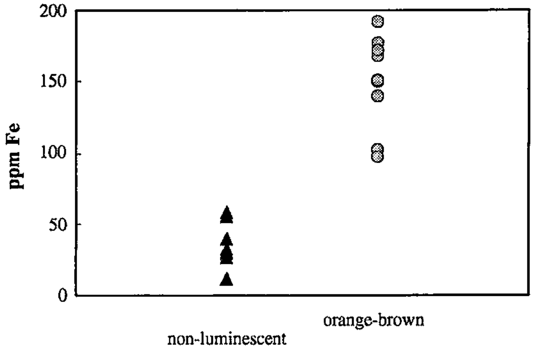

Fig. 4. Results of micro-PIXE point analyses of selected areas from rims of authigenic quartz within the Fontainebleau Sand (Oligocene, Paris Basin). Fe concentrations of the orange-brown generations are significantly higher than those of the non-luminescing ones. n = 20, detection limits approximately 5 ppm.

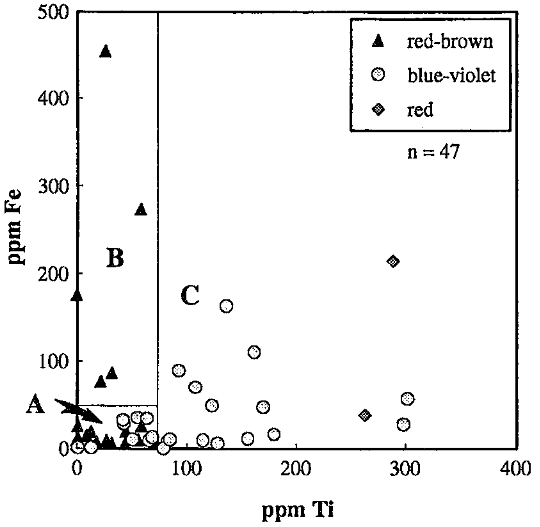

Fig. 5. CL colors and Fe and Ti concentrations of 47 detrital quartz grains from the Wiehengebirgsquarzit (Upper Jurassic, northwestern Germany) and the Fontainebleau Sand (Oligocene, Paris Basin). A. Coexisting blue-violet and red-brown CL can be observed at <75 ppm Ti and <50 ppm Fe. B. Red-brown-luminescing grains are characterized by <75 ppm Ti and higher concentrations of Fe. C. Blue-violet- and red-luminescing quartz with Ti concentrations in excess of 75 ppm.

As for the causes of the CL in quartz, the results do not unequivocally prove that the observed CL colors are activated by Ti and Fe. Despite the advantages of the microsampling technique, relative to bulk-mineral analyses, the observed trace-element contents may still reflect submicroscopic inclusions rather than incorporation of Ti and Fe into the structure.

## CONCLUSIONS

1. Proton Induced X-ray Emission (PIXE) analysis, having high lateral resolution (<10 μm) and exceptionally low detection-limits (<10 ppm), yields interpretable information that can be applied to diagenetic and provenance studies of sandstone.
2. The overgrowths of diagenetic quartz in the Fontainebleau Sand (Oligocene, Paris Basin) contain domains with orange-brown CL and nonluminescing zones. The former have considerably higher Fe concentrations (98 – 192 ppm) than the latter type (12 – 59 ppm). These differences in trace-element abundances may reflect variations in redox conditions within a shallow freshwater aquifer.
3. The previously reported qualitative correlation between CL colors of detrital quartz grains and their Ti and Fe concentrations is supported by our PIXE data for sandstones of variable ages and locations (Wiehengebirgsquarzit, Upper Jurassic, northwestern Germany; quartzitic lenses within the Fontainebleau Sand, Oligocene, Paris Basin). Iron is more abundant in red-brown-luminescing quartz (up to 455 ppm), whereas increased Ti concentrations (up to 298 ppm) are confined to blue-violet- and red-luminescing grains. This observation may help to distinguish between quartz grains from magmatic and metamorphic sources, and is thus of importance for studies of sandstone provenance.
4. Despite the high potential benefits of the PIXE microsampling technique for diagenetic and provenance studies, the role of the observed trace-elements as CL activators remains enigmatic. In many cases, the observed concentrations may reflect submicroscopic mineral or fluid inclusions rather than the presence of these elements in the mineral's structure. For a definite proof of CL activation in quartz by trace elements, future investigations should combine trace-element analyses with quantitative CL techniques, such as the high-resolution spectrometric analysis ("HRS–CL"; *cf.* Habermann *et al.* 1996).

## ACKNOWLEDGEMENTS

The development of the Bochum proton microprobe for routine analyses of mineral and rock samples has been financially supported by the Deutsche Forschungsgemeinschaft (grant #Ve112/6) and the Land Nordrhein-Westfalen. We are grateful to R.A. Mason, M.R. Owen and M. Pagel for their thorough reviews and for numerous suggestions that greatly improved the manuscript.

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*Received September 15, 1995, revised manuscript accepted May 16, 1996.*