Mineralogical Magazine, April 1999, Vol. 63(2), pp. 165–177

Magmatic and metasomatic processes during formation of the Nb-Zr-*REE* deposits Khaldzan Buregte and Tsakhir (Mongolian Altai): Indications from a combined CL-SEM study

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ABSTRACT

Cathodoluminescence (CL) imaging and spectroscopy, as well as backscattered electron imaging, were used to assign the occurrence of several mineral phases and rock structures in altered nordmarkites and calcite-bearing granites from the Nb-Zr-*REE* deposits from Khaldzan Buregte and Tsakhir (Mongolian Altai) to three events: (1) intrusion of barren nordmarkites; (2) intrusion of small bodies of calcite-bearing granites with metasomatic alteration of the wall-rocks; and (3) alteration by F-rich fluids.

Unusual red and yellow CL caused by Fe^{3+} and Mn^{2+} emission centres were detected in microcline and albite. Fe^{3+} centres were also established (along with others) in quartz, zircon, and possibly in fluorite.

Magmatic and metasomatic rock structures and internal structures of the minerals coexist in the samples. The primary magmatic features were in part preserved during alteration. In contrast, the internal and the centre structures may be changed during alteration even in non-replaced mineral phases. Euhedral minerals may be formed by secondary processes as shown for lath-shaped albite. The occurrence of pseudomorphs, the inheritance of elements during replacement, and the mechanical effects of secondary minerals on earlier mineral phases during metasomatic growth are proposed as criteria for the reconstruction of the mineral succession in altered rocks. Snowball structures may be formed as a result of metasomatic alteration rather than as a magmatic intergrowth.

Keywords: rare metals, alkaline rocks, cathodoluminescence, Mongolian Altai, Khaldzan Buregte, alteration, pseudomorphs.

Introduction

The genesis of the unusual Nb-Zr-rare earth element (*REE*) mineralisation which is related to alkaline granitic magmatism is still under discussion. At present, the most thoroughly investigated deposits of this type (Strange Lake, Thor Lake, etc.) are located in Canada (see Richardson and Brikett, 1995 for short review). A main point of controversy is whether the enrichment of exotic elements (Nb, Ta, Zr, Hf, *REE*, Y, F, U, Th, Be, Li, Rb, Sr, Sn, W, Pb, Zn, As, Ag and Ni) is caused by magmatic fractionation or metasomatic alteration processes. For the deposits of the Khaldzan Buregte group in the Mongolian Altai, discussed in more detail in this paper, Kovalenko and co-workers (Kovalenko *et al.*, 1985, 1989, 1992, 1995) favour an exceptional magmatic mechanism of formation. In contrast, Andreev and co-workers (Andreev *et al.*, 1994; Andreev and Ripp, 1996) concluded that the ore mineralisation is restricted to metasomatic alteration zones.

As we have shown earlier (Kempe and Dandar, 1995), the ore-bearing rocks exhibit mineralogical and geochemical characteristics typical of both carbonatites (enrichment of Zr, Nb, Sr, light *REE* [*LREE*], Pb, Zn, high Nb/Ta and Zr/Hf ratios, association calcite-zircon-pyrochlore or ferguso-nite) and Li-F granites (enrichment of Li, F, Rb, Sn, W, heavy *REE* [*HREE*], Y, Be, negative Eu anomalies, association fluorite-Sn-rutile-Li-mica - bertrandite). Detailed mineralogical and isotope investigations have enabled us to distinguish three main geological events of formation, separated in time but occurring in overlapping areas (Kempe *et al.*, 1997*a*; Kempe *et al.* 1998, in prep.). The intrusion of barren, large nordmarkite bodies at 423 ± 12 Ma (K-Ar ages of amphiboles) was followed by the emplacement of small bodies of calcite-bearing granites at 396 ± 1 Ma (U-Pb metasomatic zircon ages). Fluids related to the second event gave rise to strong alteration of the granites themselves as well as to alteration of the surrounding rocks (nordmarkites, dolerites, and granites). At 325 ± 14 Ma (Sm-Nd fluorite isochron age), the central parts of the deposits were overprinted by metasomatic processes caused by F-rich fluids. In the vicinity of the Khaldzan Buregte massif, we have not found magmatic rocks related to these F-rich fluids. However, the alteration event overlaps in time with the intrusion of granites of the large Kharkhirin massif to the north and the formation of F-rich W-(Sn-Be) deposits to the west in the eastern part of the Mongolian Altai.

Consequently, both magmatic and metasomatic processes seem to play an important role in the formation of the Nb-Zr-*REE* deposits at Khaldzan Buregte. The aim of the present study is to verify by application of cathodoluminescence (CL) imaging and spectroscopy as well as scanning electron microscope (SEM) techniques which mineral phases and rock structures are related to the magmatic and metasomatic processes described above. Criteria for establishing the succession of minerals in altered rocks using these methods are discussed.

Geological setting, petrographic characteristics of the samples, and description of methods

Geological setting

The Nb-Zr-*REE* deposits Khaldzan Buregte and Tsakhir as well as some smaller occurrences are located in the endo- and near exo-contact of the large Khaldzan Buregte alkaline massif extended around 20 km to the north from 48° 20′N and 92° 00′W in the Mongolian Altai. At present time, both deposits are under exploration. Estimated resources are 600,000 t niobium oxide, 35,000 t tantalum oxide, 4,000,000 t zirconium oxide, 1,000,000 t rare earth oxides, and about 100,000 t yttrium oxide for Khaldzan Buregte and 800,000 t zirconium oxide for Tsakhir, respectively. The geological map presented here (Fig. 1) is the result of a combined Landsat data interpretation with ground check. For detailed maps of the deposits based on the magmatic concept of deposit formation, the reader is refered to the publication of Kovalenko *et al.* (1995).The massif is part of a chain of alkaline intrusions in Western Mongolia generally arranged north-south within a palaeoarc between the Lake tectonic zone to the east and the Khovd zone to the west, just on the eastern borderline of the Mongolian Altai mountains. Wall-rocks consist of Cambrian volcanics, sediments, and granites. To the south the massif is partly covered by Devonian volcanics. Barren, coarse-grained alkaline magmatic rocks (syenites to alkaline granites, mainly nordmarkites) containing at least weakly mineralised pegmatites represent more than 90% of the outcrop of the massif. The Khaldzan Buregte deposit is a cone-shaped ore body and consists of the sheared intrusion of calcite-bearing granites and strongly altered and mineralised nordmarkites and pegmatites. The main ore minerals are zircon and other zirconium silicates as well as pyrochlore. The Tsakhir deposit is represented by vein-like zones of metasomatic alteration tending NW. The central part of the metasomatic bodies consists of zircon- and fergusonite-bearing calcite-epidote-quartz metasomatites. The alteration involved a dolerite body of uncertain age situated on the northern exo-contact of the Khaldzan massif and (on a smaller scale) Ordovician (?) granites and the nordmarkites of the alkaline intrusion complex. Metasomatic alteration events caused a shift in the geochemical signature of the rocks at Khaldzan and Tsakhir. This may be shown, for example, for the *REE*-distribution patterns including the occurrence of negative Eu anomalies (see Fig. 2 and Table 1), for the Rb, Y, and Nb contents, and for U/Th ratios (Kempe *et al.*, 1996; Kempe *et al.*, 1998, in prep.).

The CL and SEM studies were focused on the magmatic and alteration structures of the rocks and minerals of the nordmarkites from Tsakhir and Khaldzan and of the calcite-bearing granite from Khaldzan Buregte. The ores of the Tsakhir deposit located mainly in dolerites are clearly of metasomatic origin according to the geological position and the structure of the ore bodies (Andreev *et al.*, 1994) and are therefore not included in the present CL study. Samples of weakly to strongly altered nordmarkites from

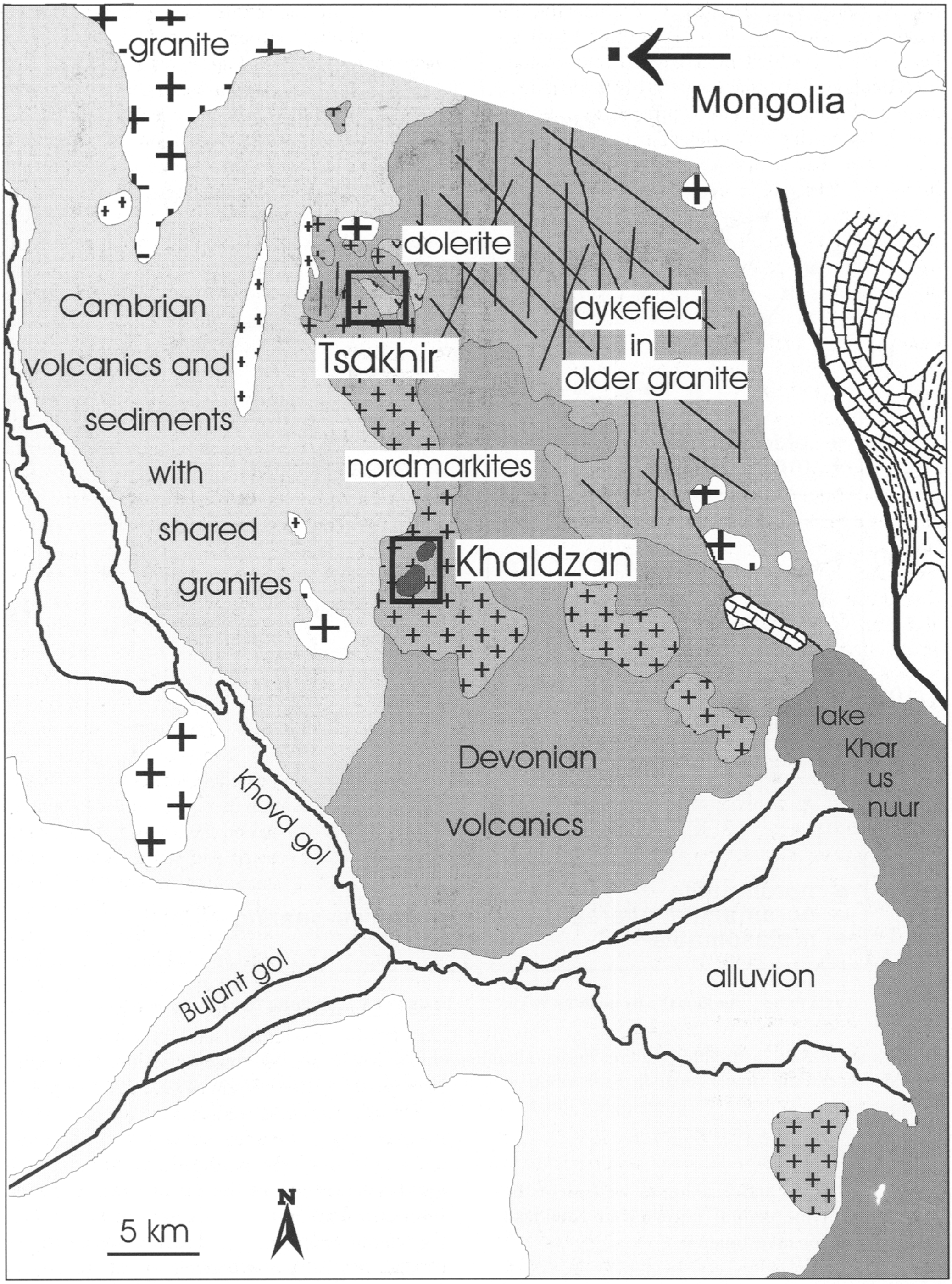

FIG. 1. Geological map of the Khaldzan Buregte massif with the location of the Nb-Zr-*REE* deposits Tsakhir and Khaldzan Buregte according to the interpretation of Landsat images and ground check. The sheared calcite-bearing granite intrusion of Khaldzan Buregte is the small black area near the centre of the figure.

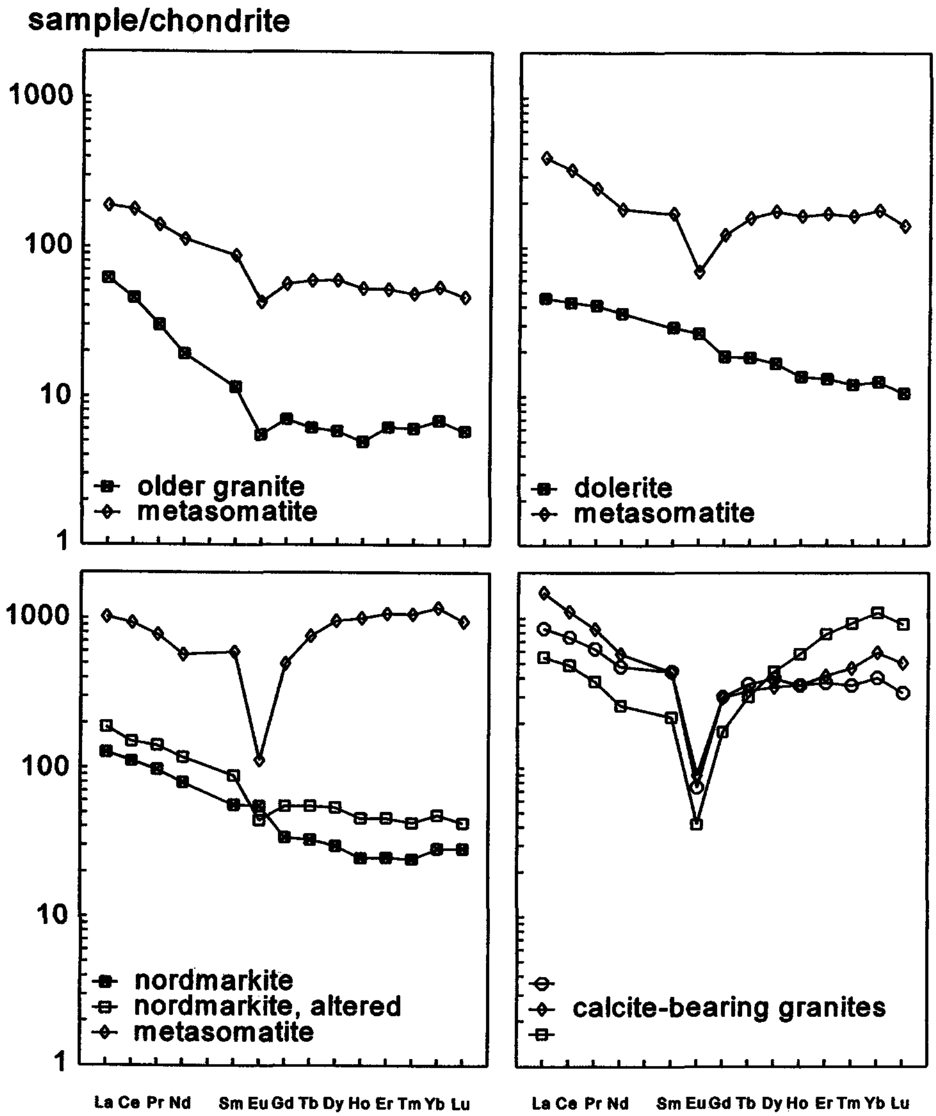

FIG. 2. Changes of *REE* distribution patterns during alteration of Ordovician (?) granite (upper left), dolerite (upper right), and nordmarkite (lower left). *REE* distribution patterns of altered calcite-bearing granite from Khaldzan (lower right). Related ICP-MS data see Table 1.

Khaldzan Buregte and Tsakhir as well as of the granites from the central intrusion at Khaldzan were chosen for investigation.

Petrographic sample description

General petrographic characteristics of the investigated rocks are summerised in Table 2. Fresh samples of nordmarkite consist of K-Na-feldspar, quartz, hastingsite-kaersutite series amphibole, and accessories. The K-Na-feldspar shows perthitic structures possibly partly enlarged during later albitisation. In altered samples, amphibole is replaced by aegirine. Small grains of albite and quartz are visible on the grain boundaries between the primary K-Na-

TABLE 1. *REE* contents in weak and strong altered rocks from the Khaldzan Buregte and Tsakhir deposits (ppm, ICP-MS data by XRAL, Canada)

Rock type	Older granite	Older granite altered	Dolerite	Dolerite, altered	Nord-markite	Nordmarkite, weakly altered	Nordmarkite, strongly altered	Granite with calcite	Granite with calcite	Granite with calcite
La	19.0	58.7	14.2	125	39.4	71.3	316	170	264	460
Ce	38.2	150	35.9	280	93.0	175	782	408	627	935
Pr	3.60	16.9	4.90	30.1	11.6	21.4	93.2	45.6	75.1	102
Nd	11.5	67.8	21.7	109	47.6	87.2	340	157	285	346
Sm	2.30	17.5	5.80	33.8	11.2	22.6	118	43.9	88.2	87.4
Eu	0.40	3.08	1.94	5.03	4.02	4.28	8.20	3.05	5.44	6.54
Gd	2.10	16.9	5.60	36.9	10.1	21.7	148	52.7	90.1	88.6
Tb	0.30	2.90	0.90	7.80	1.60	3.80	37.0	14.7	17.9	16.1
Dy	1.80	18.5	5.20	54.5	9.20	24.8	297	137	123	108
Ho	0.36	3.83	1.00	12.0	1.79	5.41	72.8	42.2	26.1	26.2
Er	1.30	10.9	2.80	35.8	5.20	17.2	225	165	78.4	87.0
Tm	0.20	1.60	0.40	5.40	0.80	2.80	35.1	30.7	11.8	15.3
Yb	1.30	10.2	2.40	34.1	5.40	19.5	223	208	76.2	112
Lu	0.18	1.43	0.33	4.38	0.88	2.84	29.4	28.3	9.87	15.6

TABLE 2. General petrographic characteristics of rock samples from the Khaldzan Buregte and Tsakhir deposits investigated by optical microscopy, optical CL, and SEM

Rock type	Nordmarkite	Calcite-bearing granite
Colouration	reddish to greyish	white to reddish
Structure	medium to coarse grained hypidiomorphic	medium grained hypidiomorphic
Primary minerals	perthite (70–85%) quartz (5–10%) amphibole (5–10%)	microcline (40–60%) quartz (20–30%) aegirine (3–10%) calcite (5–10%)
Primary accessories	zircon magnetite ilmenite apatite	zircon (together with secondary zirconium minerals up to 15%)
secondary minerals	quartz albite aegirine annite titanite fluorite hematite pyrochlore gittinsite zircon rutile neptunite bertrandite	albite (10–30%) *REE*-F carbonates fluorite hematite pyrochlore gittinsite armstrongite (Na) rutile murataite

feldspar, quartz, and amphibole. In the perthite are many tiny mica flakes. It is not always clear, whether increased zircon contents in altered samples are related to the alteration or to fluctuations in the zircon content in the primary nordmarkites. A characteristic feature of the strongly altered nordmarkites (as well as of the calcite-bearing granites) from the Khaldzan Buregte deposit is the presence of pseudomorphs. Pseudomorphs of quartz and zircon with little albite, pyrochlore, and rare gittinsite are typical. We found that gittinsite was not the main Zr-mineral in these pseudomorphs and in the ores, contrary to the description of Kovalenko *et al.* (1995). Zircon-quartz pseudomorphs in altered nordmarkites were formed after mafic minerals (amphibole and aegirine) and not after elpidite (Kovalenko *et al.*, 1995). Elpidite was not found during our study. Altered nordmarkites contain a lot of additional accessory minerals (see Table 2). As in other deposits of the Nb-Zr-*REE* type, the mineralogy of the altered rocks is very complex (Andreev *et al.*, 1994; Kartashov *et al.*, 1994; Kovalenko *et al.*, 1995; Kempe *et al.*, 1996). The occurrence of neptunite (after fibrous aegirine) and of fluorite-bertrandite ores in strongly altered nordmarkites on the flanks of the Khaldzan Buregte ore body were established during our investigations (Kempe *et al.*, 1997*a*).

The central intrusion of peralkaline granite at Khaldzan is made up of rocks consisting of rounded microcline grains (often with snowball-like intergrowths with albite), quartz (sometimes also with snowball-like intergrowth with albite), euhedral aegirine, and calcite in interstices between microcline and quartz (not described by previous authors). The calcite often contains zircon, gittinsite, and Na-bearing armstrongite (total Zr minerals: 3–15%). Lath-shaped albite intersecting grain boundaries of K-feldspar, quartz, and calcite is also typical of this rock-type. The replacement of calcite by fluorite and of zircon by gittinsite were established in most of the investigated samples. In the exo-contact, small dykes and volcanic roof remnants with analogous characteristics were found. It is often difficult to distinguish between the calcite-bearing granite and the mineralised nordmarkite within the alteration halo, especially during field work. The presence of snowball structures of K-feldspar and quartz, the occurrence of early calcite and a higher Al content (>10 wt.% Al_2O_3) were applied as criteria in this study.

Methods

Polished thin-sections were used for optical microscope investigations (transmitted light) and CL imaging on a 'hot cathode' CL microscope (14 kV accelerating voltage, 10 $\mu A/mm^2$ current density). To prevent the build-up of electrical charge during CL operations, carbon-coated thin sections were used. Luminescence features were detected simultaneously during electron irradiation in a time interval of up to 10–15 min in order to detect time-dependent variations in the CL behaviour of different minerals. Documentation of variations in the luminescence was realized using an attached NICON camera and Kodak Ektachrome 400. CL spectra (horizontal resolution of the spot about 30 μm) were obtained by means of a digital triple-grating spectrograph (theoretical resolution 0.5 nm at 600 nm) coupled with a liquid nitrogen cooled, Si-based CCD detector. The detector was attached to the microscope by a silica-glass fibre guide (Neuser *et al.*, 1995). CL spectra were measured using standardized conditions (wavelength calibration by a Hg lamp, accumulation time 10 s). To prevent any falsification of the CL spectra due to electron bombardement, all spectra were taken starting from non-irradiated sample spots.

SEM investigations were carried out on the same thin-sections using a Jeol JSM 6400 for secondary electron (SE) and backscattered electron (BSE) imaging. The SEM was equipped with an Oxford MonoCL 1 system used for CL imaging and a Tracor (Noran) series II EDX system for X-ray analysis. The SEM was mostly operated at 20 kV with a 0.6 nA beam current. For BSE imaging of zircon and other ore minerals, up to 25 kV and 2 nA and for detection of CL images 20 kV and 1 nA were used.

Results

The rock-forming minerals from the samples investigated show a CL behaviour unusual for magmatic environment. The CL of quartz and K-feldspar is often unstable and shows decreasing intensities with time. Documentation of images and detection of spectra are therefore sometimes complicated.

K-feldspar

The CL of the microcline (nearly pure $KAlSi_3O_8$ with less than 1 mol% albite) varies strongly even within one grain. The dominating colour in the weakly to strongly altered samples of nordmarkite and granite is reddish to bright yellow, somtimes with a greenish tint (Plate 5). 'Normal' bluish luminescing areas were found only in the weakly altered samples of nordmarkite within parts of microcline grains free of albite (Plate 5A). The bluish luminescence is more stable under the electron beam, but quenched when microcline is enriched in tiny flakes of mica (pure annite as proved by EDX analyses). It is well-known that annitisation of the Fe-rich alkaline wall-rocks is a typical feature of some types of carbonatite intrusions (Samojlov, 1977). On the boundary to the albite-rich parts of the microcline grains, bluish CL exhibits a violet tinting (Plate 5A). Bluish luminescing areas, occassionally showing primary, oscillatory growth zoning, may be interpreted as remains of the primary magmatic luminescence.

The time-resolved observation of the reddish to yellow luminescence reveals that the colour is a superposition of two signals. The red emission is quenched with time, whereas the yellow CL remains stable (Plate 5A–E). Red CL is more intensive and long-lived in weakly altered nordmarkites than in strongly altered samples and in the calcite-bearing granite. In nordmarkites, reddish to yellow luminescing areas in microcline are rich in secondary annite. The distribution of the red as well as of the yellow centres and the kinetic of the quenching of the red CL are not homogeneous within the grains and reflect a patchy internal structure typical of minerals in metasomatic altered rocks. CL spectroscopy allows the interpretation of the yellow and of the red emission bands at 585 and 713 nm (Fig. 3) as related to the Mn^{2+} and Fe^{3+} centres, respectively, in analogy to centres in plagioclases (Telfer and Walker, 1978).

Quartz

The CL of quartz is generally weak except the small secondary grains in altered nordmarkites showing a red luminescence colour (Plate 5A). The large primary quartz grains in the altered nordmarkites exhibit a stable dull violet CL, sometimes with visible oscillatory zoning or traces of small cracks. Spectral investigation proves that along with the well-known composite blue emissions around 450 nm and the emission at ~620 nm even in this quartz type low amounts of the Fe^{3+} centre are detectable (Fig. 3). The emission band at 707 nm related to Fe^{3+} was described by Pott and Mc Nicol (1971) for synthetic quartz samples. In the mineralised samples from the exo-contact of the Khaldzan Buregte granite intrusion, a characteristic yellowish luminescing halo, due to radiation, is visible around pyrochlore crystals (Plate 5D). In the pseudomorphs intergrown with zircon, the CL of quartz is brownish (Plate 5C).

Most of the quartz in the calcite-bearing granite shows a fine oscillatory growth zoning and a weak brownish colour under CL. However, some parts of the quartz have an unstable inky blue luminescence revealing a cloudy internal structure (Plate 5F), which were interpreted as areas of metasomatic quartz growth.

Albite

A stable and unusual intensive red luminescence was found for albite (less than 5 mol% anorthite) in all samples investigated (Plate 5). Red CL of feldspar was found to be typical of fenitization related to alkaline or carbonatitic rocks (Rae and Chambers, 1988; McLemore and Modreski, 1990) and was also reported for the Strange Lake complex, Canada (Salvi *et al.*, 1995, pers. comm.). In some samples of the calcite-bearing granite, CL reveals a yellow and red patchy internal structure (Plate 5F). High-resolution SEM-CL imaging proves that the same type of internal structure may also be found in red luminescing albite from other samples (Fig. 4A). The red colour is caused by a band centred at 720 nm (Fig. 3) and may be assigned to the Fe^{3+} centre (Telfer and Walker, 1978). The uneven grain boundaries of the 'perthitic' albite in the microcline (Plate 5A,B), of the small albite grains between quartz, microcline, and amphibole in the altered nordmarkite (Plate 5A), and of some of the lath-shaped albite crystals in calcite-bearing granite crosscutting grain boundaries of microcline, quartz, and calcite (Plate 5E) suggest that at least in part albite is of metasomatic origin.

Zircon

In weakly altered nordmarkite, zircon exhibits under CL a primary, oscillatory growth zoning (Plate 5B), which is also visible in the BSE images (Fig. 4C). The luminescence colour is greenish-blue with some narrow yellow zones. Primary zircon from the calcite-bearing granite intergrown with quartz or calcite shows similar CL behaviour but with more coarse zoning

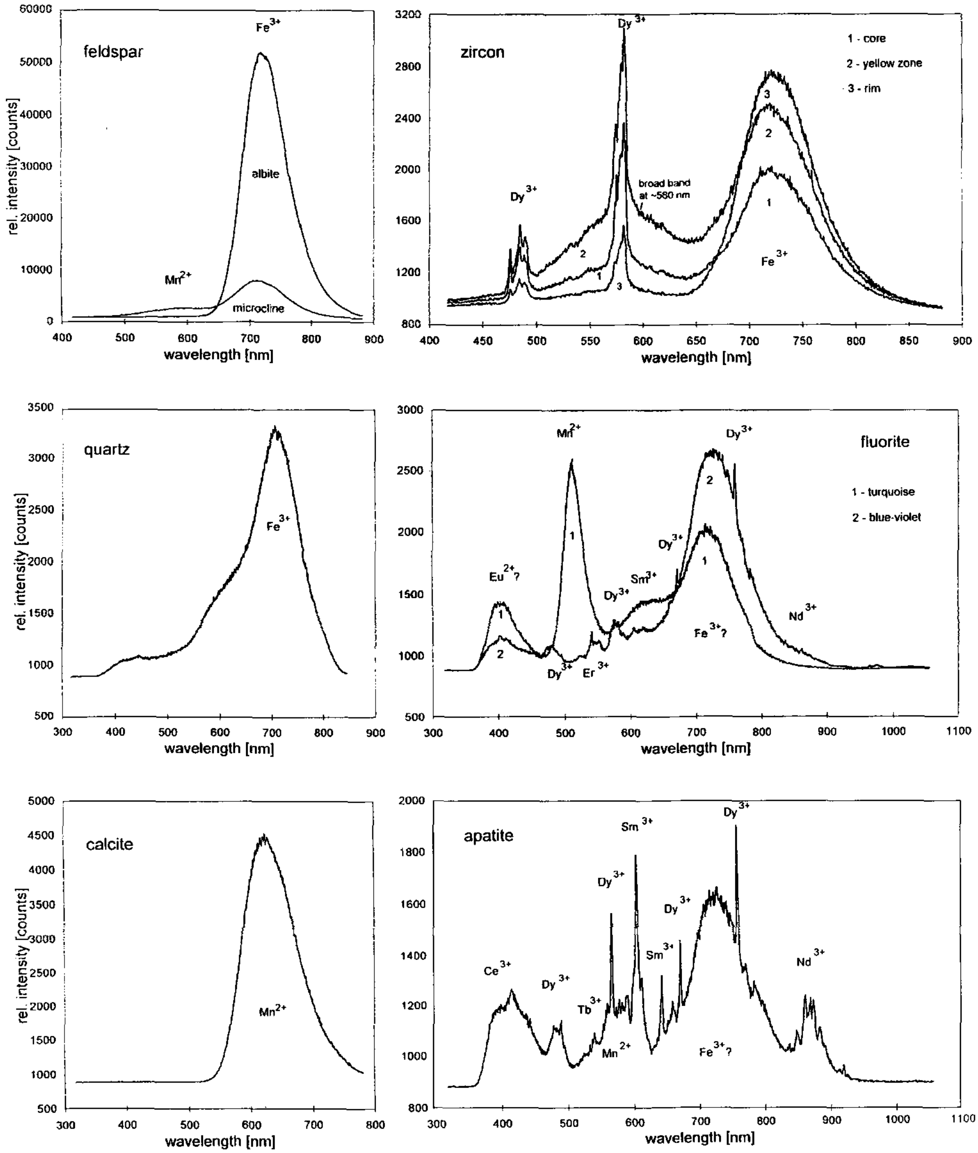

FIG. 3. CL spectra of minerals from altered nordmarkites and calcite-bearing granites from Khaldzan Buregte and Tsakhir (see text for further explanations).

(Plate 5F). In nordmarkite, CL is often quenched at the rim and the primary zoning is destroyed as detected in both CL and BSE images (cf. Plate 5B and Fig. 4C). Spectra obtained for the crystal in Plate 5B show strong emission of Dy^{3+} centres causing greenish tinting of the CL colour. The yellow emission in the narrow zones is related to the known band centred near 580 nm. An increasing intensity of the Fe^{3+} emission from the core to the rim correlating with increasing Fe content (up to 0.5 wt.% Fe) in the mineral was found (Fig. 3). It was not possible to record the band at 430 nm dominating the bluish CL colour with the CCD detector used in the present study.

In strongly altered samples, zircon CL is not detectable and patchy internal structures like in

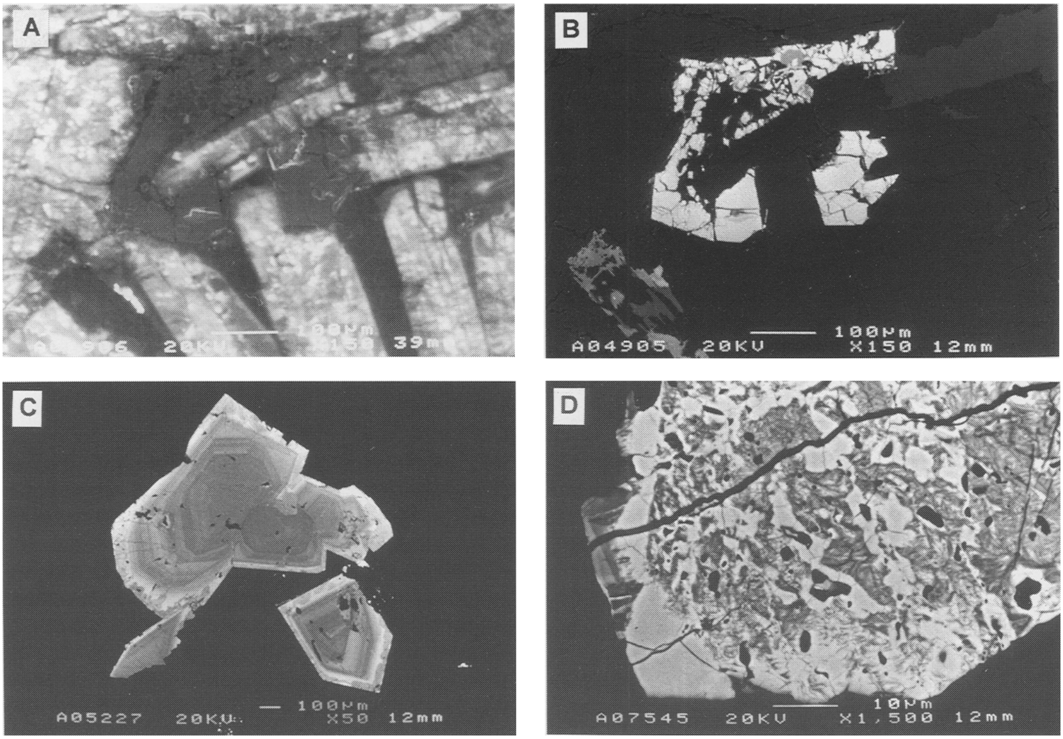

FIG. 4. Internal structure of minerals from Khaldzan in CL and BSE images taken in SEM. (A) Secondary albite with patchy internal structure (high-resolution SEM-CL image). (B) Remnant pyrochlore after secondary albite growth in microcline (BSE image of the same area as in A). (C) internal structure of luminescing zircon in altered nordmarkite (BSE). At the rim, primary oscillatory zoning is replaced. (D) patchy internal structure of a non-luminescing zircon in strong altered nordmarkite (BSE).

Hf-rich zircons from altered Li-F granites (Kempe *et al.*, 1997*b*) are visible only in the BSE images (Fig. 4D). Such zircons are enriched in Ca, Fe (>1 wt.%), and sometimes also in U, Th, Y, and *REE*. High trace element concentrations possibly cause CL quenching. The zircon in the zircon-quartz pseudomorphs appears brownish under CL, but this colour is possibly related to the brownish colouration of the mineral (Plate 5C).

Apatite

Bluish violet to cream-coloured CL (Plate 5B) and occasional primary, oscillatory growth zoning are typical of apatite detected only in weakly altered samples of nordmarkite. As revealed by the CL spectrum, the colour is the result of the superposition of intensive, sharp line groups of *REE* centres (Dy^{3+}, Sm^{3+}, Eu^{2+}, and Ce^{3+}) and a weaker but broad emission band of Mn^{2+} at 570–580 nm.

Calcite

The intensive orange luminescence of calcite in the granite from the Khaldzan Buregte deposit is caused by the emission of the Mn^{2+} centre. This can be proved by the distinct phosphorescence of the centre and by the detected luminescence spectrum with a band at 620 nm (Marfunin, 1979; see Fig. 3). The Mn content found in this calcite reaches 3.5 wt.%. *REE* were not detected, either by CL or by EDX.

Fluorite

One of the most common secondary minerals in the rocks investigated is fluorite (Plate 5D,E). Its CL colour varies from bright turquoise to bluish-violet. Mostly, fluorite occurs intergrown with *REE*-F carbonates in bright luminescing fine-grained aggregates, replacing other minerals (Fig. 5C). Oscillatory zoned bluish violet lumines-

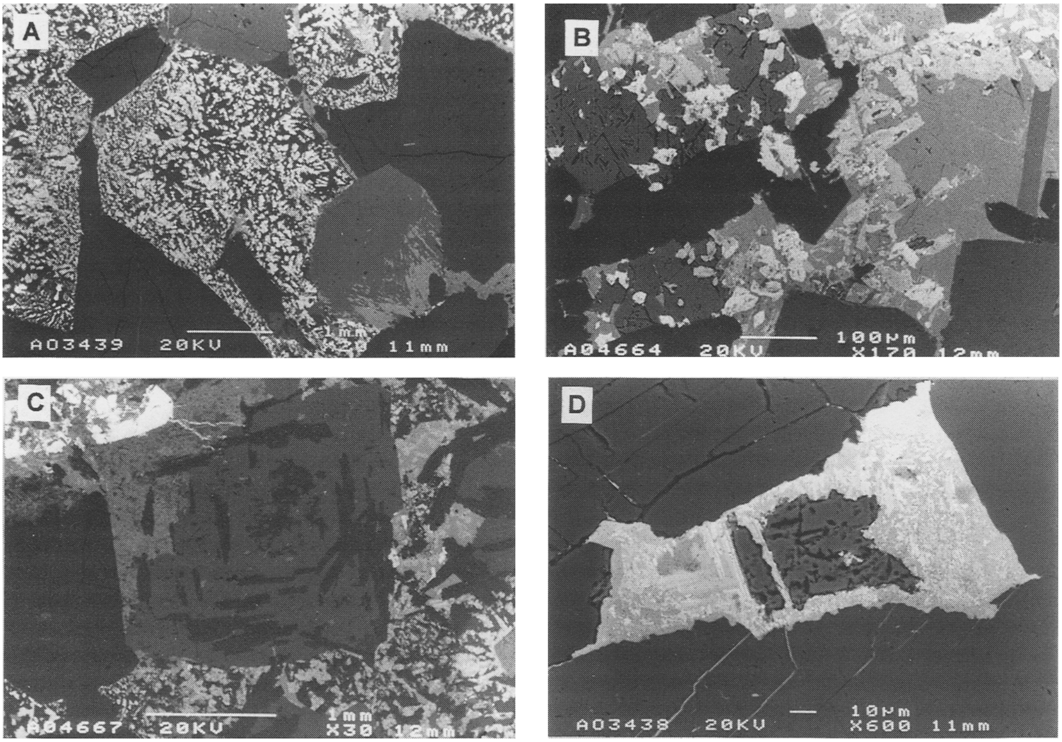

FIG.5. Pseudomorphs from rocks of the Khaldzan Buregte deposit (BSE images). (A) dendritic zircon (white) -quartz pseudomorphs after amphibole and aegirine and replacement of microcline by radiate fluorite (greyish) in nordmarkite. (B) pseudomorphs of armstrongite and gittinsite (greyish) after zircon (white) and calcite (with distinct cleavage) in the calcite-bearing granite. Dark minerals are albite (black) and microcline (dark greyish). (C) Fluorite-*REE*-F carbonate intergrowth replacing snowball microcline in the calcite-bearing granite. Around the microcline crystal, Zr silicates are visible. On the upper left -pyrochlore (white). (D) Pseudomorph of synchysite and bastnäsite after calcite in the calcite-bearing granite.

cing crystals are rare (Plate 5D). Cathodoluminescence spectra of the latter type contain bands and line groups of Eu^{2+}, Dy^{3+}, Er^{3+}, Nd^{3+}, and Sm^{3+} (Fig. 3). ICP-AES investigation showed high enrichment of all *REE* (up to 0.n wt.% rare earth oxide) in this fluorite type (Kempe *et al.*, 1995). The bright turquoise luminescence is caused by emission of Eu^{2+} (?) and Mn^{2+} centres. The intensity of the REE^{3+} line groups is very low (Fig. 3). The Mn^{2+} peak, normally centred at 500 nm, is shifted to 510 nm, possibly due to the high Sr content in the fluorite (up to 8 wt.% Sr). In both fluorite spectra, a broad band at 725 nm was detected. If this is not an artifact from the neighbouring albite luminescence (note the slight shift of the emission band from 720 to 725 nm), the signal may be possibly assigned to a Fe^{3+} centre in fluorite. The detected Fe content in fluorite varies between 2500 and 7000 ppm (ICP-MS data, Kempe and Plötze, 1997, unpubl.).

Pseudomorphs

The succession of minerals in a rock is often derived from the observation of the apparent phase relations. For example, an euhedral mineral enclosed in another mineral is considered to be formed before or at least together with the latter. Such an approach, however, leaves aside possible solid state reactions with replacement of mineral phases documented, for example, in the formation of pseudomorphs.

Beside the zircon-quartz pseudomorphs after amphibole and aegirine, many other pseudomorphs were found during our study by SEM investigation. Some of the most important (fluorite after microcline; gittinsite and amstrongite after zircon and calcite; fluorite and *REE*-F carbonates after snowball microcline; and *REE*-F carbonates after calcite) are shown in Fig. 5. Incomplete formation of pseudomorphs reveals important information on both the starting and end products of solid state reactions in multistage ores. As we have discussed elsewhere, another criterion for establishing replacement processes may be the detection of elements inherited from the original mineral (Kempe and Sorokin, 1988). An additional criterion may be the mechanical effect of the replacing mineral on surrounding minerals during metasomatic growth.

Pyrochlore

The main carrier of Nb in the Khaldzan Buregte deposit is pyrochlore. Euhedral crystals were found in microcline in the calcite-bearing granite and in the strongly altered nordmarkite using BSE imaging combined with EDX. Pyrochlore crystals are often crushed in pseudomorphs (e.g. of the zircon-quartz type). Moreover, pyrochlore crystals were destroyed by albite (Fig. 4A,B). This fact proves again the secondary origin of the albite in the calcite-bearing granite. The euhedral shape of most of the albite crystals is not a result of early formation, but is caused by the behaviour of the mineral during crystal growth in the solid state. Possibly, pyrochlore in the microcline formed also later than the host mineral, because the occurrence of pyrochlore in nordmarkite is restricted to the strongly altered samples.

Snowball structures

Snowball quartz was often found in evolved granite intrusions and is commonly assigned to magmatic (eutectic) mechanisms of formation (e.g. Kovalenko *et al.*, 1995 for Khaldzan Buregte). However, our CL investigations revealed a metasomatic origin of albite including crystals in snowball microcline (Plate 6A). During the second alteration event, microcline is often replaced by other minerals, particularly by quartz (Plate 6B). Therefore, in Khaldzan Buregte the snowball quartz structures (Plate 6C) may be formed by metasomatic processes.

Discussion

The results presented here show that magmatic and metasomatic structures and features coexist in both nordmarkite and granite samples. Nevertheless, it is possible to constrain several phases of Nb-Zr-*REE* deposit formation. At the beginning, nordmarkites were formed as magmatic rocks consisting of K-feldspar (perthite), amphibole, some quartz, and typical accessories (ilmenite, magnetite, zircon, and apatite). Originally, minerals were formed in a magmatic rock structure and with magmatic internal structures (primary, oscillatory growth zoning of K-feldspar, zircon, and apatite; perthitic intergrowth of microcline and albite) as revealed by optical microscopy, CL, and BSE imaging.

The later intrusion of the fluid-saturated carbonate-rich granites led also to the formation of primary, magmatic rock structures and internal structures of the minerals in these granites (e.g. microcline, quartz, aegirine and zircon mostly showing primary, oscillatory growth zoning under CL). Additionally, a subsequent alteration of these rocks and the surrounding nordmarkites, dolerites and older granites by related fluids were induced. The most important result of nordmarkite alteration is the replacement of amphibole, finally also of aegirine, ilmenite, and magnetite and the remobilization of iron. The CL investigation proves the secondary formation of quartz and albite in these rocks. Additionally, we found secondary annite, pyrochlore, and zircon. The latter often forms typical zircon-quartz pseudomorphs replacing mafic minerals in nordmarkite. The magmatic structure of the nordmarkite is mainly preserved, but CL imaging shows that even in non-replaced minerals (microcline, quartz, perthitic albite, and primary zircon) the centre structure (newly formed Fe^{3+} and Mn^{2+} CL emission centres) and in part the internal structure (e.g. of perthite and zircon) are changed. The formation of pyrochlore, calcite and, possibly, of late lath-shaped albite in the granite intrusion may be assigned to this first metasomatic alteration. The high Mn content in calcite and the occurrence of secondary Mn^{2+} centres in microcline and albite may indicate a close relation between carbonate crystallisation in the granite and feldspar alteration in the nordmarkites.

Further formation of pseudomorphs took place during alteration of the rocks by late F-rich fluids. Fluorite replaces microcline and calcite, often together with *REE*-F-carbonates. These fluids also caused the enrichment of *HREE* and Y along with the formation of negative Eu anomalies as indicated not only by the chemical analyses of the rocks and fluorites but also by the high intensity of $HREE^{3+}$ (Dy^{3+} and Er^{3+}) CL emission lines in fluorite. It is noticable that REE^{3+} centres were not detected in early calcite, which is probably enriched in the *LREE* (La and Ce) not involved in the formation of CL centres. Some new quartz with inky blue CL was formed in the calcite-bearing granite. The origin of fluorite-bertrandite ores and of exotic minerals (e.g. of neptunite after fibre aegirine and of murataite) fall also in this phase. The replacement of a significant part of zircon in the calcite-bearing granite by gittinsite and armstrongite (Na) is especially important from the point of view of ore processing.

The results allow us to draw some general guidelines for application of optical CL, REM-CL, and BSE imaging as well as CL spectroscopy to the investigation of altered alkaline rocks. Detailed information may be obtained by optical CL for luminescing minerals as K-feldspar, quartz, albite, zircon, apatite, calcite, and fluorite. Time-resolved observation of CL is recommended for minerals with unstable CL behaviour as quartz, sometimes also K-feldspar, apatite and fluorite. Application of CL spectroscopy is unavoidable for the identification of centres causing CL emission and (in their combination) colouration in optical CL. The high-resolution SEM-CL is useful during investigation of the internal structure of luminescing minerals because the fine structure of mineral growth or alteration is often smudged in optical CL.

If CL is not observable, the internal structure is often detectable by BSE imaging in a SEM, especially in ore minerals with a high average atomic number, and first of all, in zircon. BSE imaging may be applied in all investigations of phase relations between non-luminescing minerals (in our case, amphibole, aegirine, annite, pyrochlore, amstrongite, gittinsite, etc.).

Conclusions

Detailed CL and SEM investigations support our earlier conclusions about a multi-phase formation of the Nb-Zr-*REE* deposits at Khaldzan Buregte (Mongolia). Both magmatic and metasomatic processes contribute to the extreme fractionation and enrichment of several elements. Subsequent emplacement of small bodies of calcite-bearing granites after the intrusion of large, barren nordmarkite bodies led to the formation of extensive Nb-Ta-Zr-Hf mineralisation. Related fluids caused strong alteration of the granite and sometimes intensive mineralisation of the wall rocks. This phase exhibits many geochemical and mineralogical features typical of carbonatites. During late metasomatic alteration by F-rich fluids, Nb-Zr-*LREE* ores were changed to Nb-Zr-*LREE*-*HREE*-Y(-Be) ores with negative Eu anomalies in the *REE* distribution patterns.

Our results show that primary magmatic structures of the rocks as well as those of the minerals may be partly preserved during secondary alteration. A characteristic feature of this phenomenon is the formation of pseudomorphs. On the other hand, metasomatic processes may change or delete primary internal structures even in unreplaced minerals (e.g. in zircon and microcline). Some primary mineral phases (amphibole, ilmenite, magnetite, and apatite) may be replaced completely. Magmatic structures may be also replaced (formation of fine-grained intergrowth) or slightly altered (e.g. secondary albite growth in pethitic structures in nordmarkite). CL spectroscopy proved that during alteration the centre structure of the minerals was changed, even in those which were not or only partly affected by replacement processes. Consequently, practically all minerals in the altered rocks were involved in the metasomatic solid state reactions.

The example of secondary, euhedral albite points to a possible formation of late euhedral crystals in early mineral phases. Therefore, the interpretation of apparent phase relations in rocks may yield misleading results and should be done with caution. For example, characteristic snowball structures may occur as a result of magmatic crystallisation and of metasomatic alteration processes as well.

Acknowledgements

This study was supported by a grant of the Deutsche Forschungsgemeinschaft (DFG). Authors would like to thank R.D. Neuser and D.K. Richter providing access to the spectral CL investigation at the Ruhr-University, Bochum. D. Wolf and J. Lehmann are thanked for support of the field work and of the investigations of the mineralogy of the ores. T. Pohl and K.P. Stanek assisted with LANDSAT data processing and interpretation. Field work in the Mongolian Altai was possible only with the help of our Mongolian friends whose support is also greatly acknowledged. We are very grateful to Frances Wall and Adrian Finch for critical review of the manuscript and help in improving the English.

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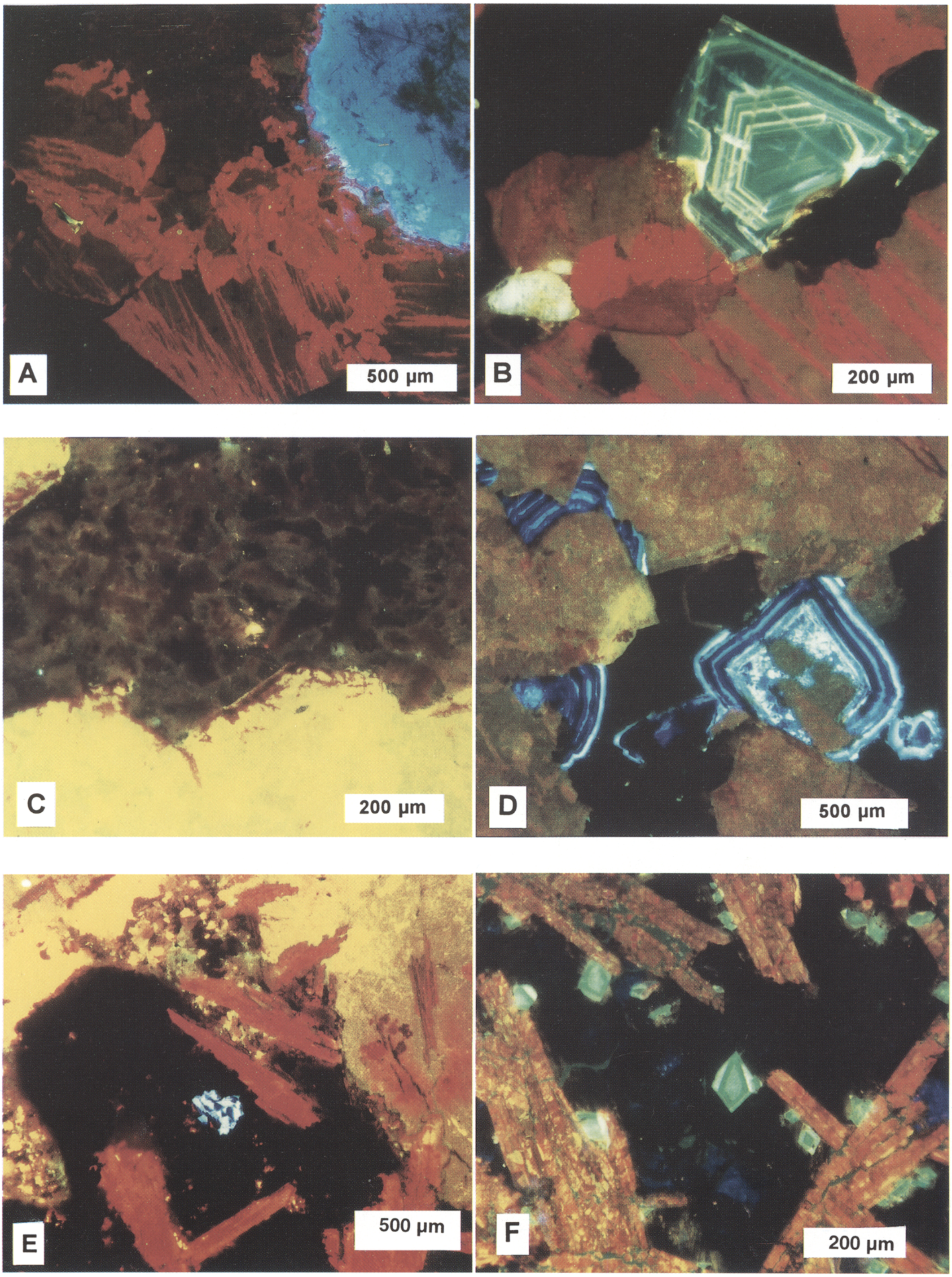
[*Manuscript received 21 September 1998*]

PLATE. 5. CL images of rocks from Khaldzan Buregte and Tsakhir: (A) primary bluish luminescence of microcline, red CL of secondary albite and quartz, and dull CL of primary quartz in altered nordmarkite. Microcline in perthite after short exposure luminesces reddish-brown. (B) primary zoned zircon with some narrow yellow zones in altered nordmarkite (CL spectra see Fig. 4). CL on the rim is quenched. After longer exposure microcline in perthite appears brownish-yellow. Grains in the lower left are apatites. (C) brownish luminescing zircon-quartz pseudomorphs in strongly altered nordmarkite. After long exposition microcline shows patchy, greenish-yellow CL except at the grain boundaries to zircon-quartz pseudomorphs. (D) secondary fluorite in strongly altered nordmarkite. Dull violet luminescence of quartz and patchy internal structure of microcline are visible. The inner parts of the fluorite crystals are intergrowth with *REE*-F carbonates, rims are oscillatory zoned (CL spectra see Fig. 4). (E) fluorite and lath-shaped albite (red CL) in quartz (dull brownish CL) and microcline (patchy yellowish) in calcite-bearing granite. Strong luminescing orange-yellowish areas are calcite, sometimes intergrown with Zr silicates. (F) primary zoned zircon and patchy yellow to red luminescing albite in quartz (partly secondary with blue CL) in calcite-bearing granite.


A
500 µm
B
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C
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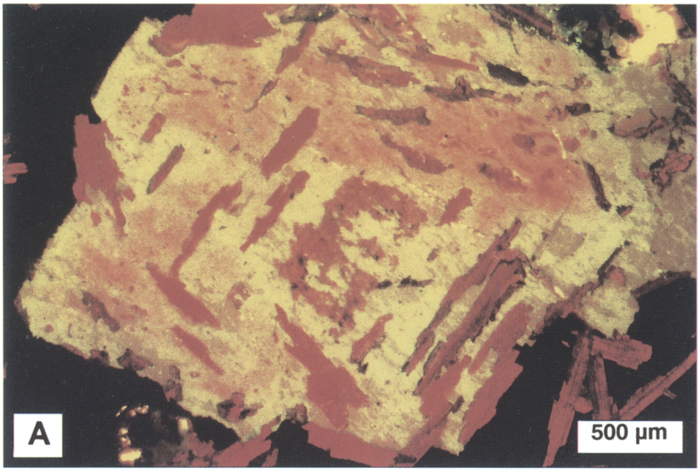
D
500 µm
E
500 µm
F
200 µm

PLATE 6. Snowball structures from the Khaldzan Buregte deposit. (A) snowball microcline (CL image). (B) Snowball microcline partly replaced by quartz (transmitted light, crossed polars). (C) Snowball quartz (transmitted light, crossed polars).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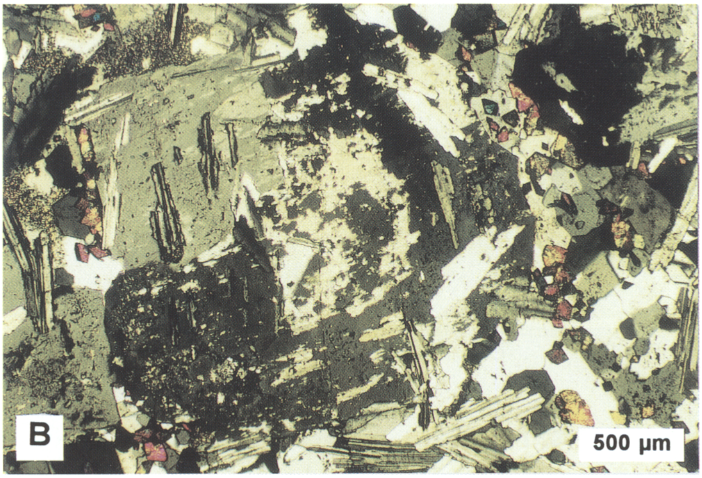
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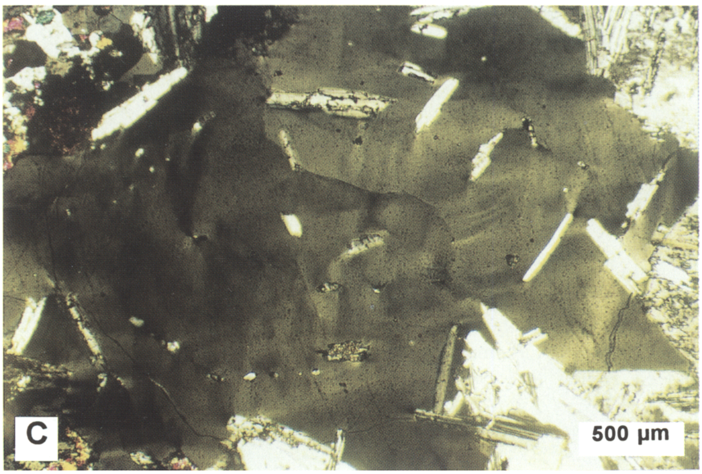
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