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Cathodoluminescence microscopy of high-temperature skarn minerals from Fuka contact aureole, Okayama, Japan

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Abstract Cathodoluminescence (CL) microscopy of high-temperature skarn minerals from Fuka, Okayama, Japan, helped to distinguish minerals having similar optical properties and their internal textures. Spurrite and tilleyite, having similar optical properties, were easily distinguished using CL microscopy. Furthermore, growth patterns could be identified in single crystals of wollastonite using CL images. Although the chemical variations corresponding to the CL variations cannot be distinguished using electron microprobe analyses, they are considered to reflect minor variations in trace element and REE contents. Thus, cathodoluminescence microscopy is a useful tool to distinguish minerals and helps us in selecting suitable sub-samples for detail studies on trace and rare earth element geochemistry.

Key words: Cathodoluminescence, spurrite, tilleyite, skarn, Fuka

Introduction

In the past few decades, the advancement of micro-analytical techniques in geochemistry has revolutionized our understanding of geological processes. However, micro-analytical techniques are often highly expensive and therefore selection of suitable samples using high-resolution microscopy and major element chemical mapping has become a prerequisite nowadays. Commonly applied techniques include Back Scattered Electron imagery (BSE) and elemental mapping using an electron microprobe. Although these techniques consume time, they are useful to understand the chemical heterogeneity in a micrometer scale. The limitations of electron microprobe analyses are usually low detection limits and difficulty in identifying heterogeneity in trace and rare earth elements in minerals and rocks samples.

In this study we demonstrate the usefulness of cathodoluminescence (CL) microscopy in identifying minerals and their chemical heterogeneity. As an example, we apply CL microscopy to observe the high-temperature skarn minerals from the contact aureole in Fuka, Okayama prefecture. We compare the mineral chemistry with the help of cathodoluminescence images and discuss the possible causes for intra-grain chemical variations.

Instrumentation and methodology

There are two types of cathodoluminescence (CL) analytical systems commonly used: 1) CL attachment to a SEM or EPMA or TEM and 2) CL attachment to an optical microscope (Pagel *et al.*, 2000). In this study, we describe the later type of CL instrument. Electron beam is usually generated by an electric discharge between two electrodes under moderate vacuum condition (~100 Pa) (Marshall, 1988). The beam is then focused and directed toward the sample using a magnetic field.

The CL system (ELM-3R LUMINOSCOPE®) at Shizuoka University comprises of an electron gun which can generate an electron beam using an accelerating voltage up to 30 keV and a beam current of 2 mA. This unit is fixed on the stage of a normal petrological microscope (Nikon® E600 POL) equipped with digital photographic attachment (Nikon® COOLPIX 995).

Polished thin section samples are placed in the X-Y stage and the domain for CL imagery is located using polarized optical microscopy. Under moderate vacuum conditions (~100 millitorr), electron beam is directed towards the sample using a magnetic field produced by the bar magnets placed outside the window of the vacuum chamber. The beam is focused

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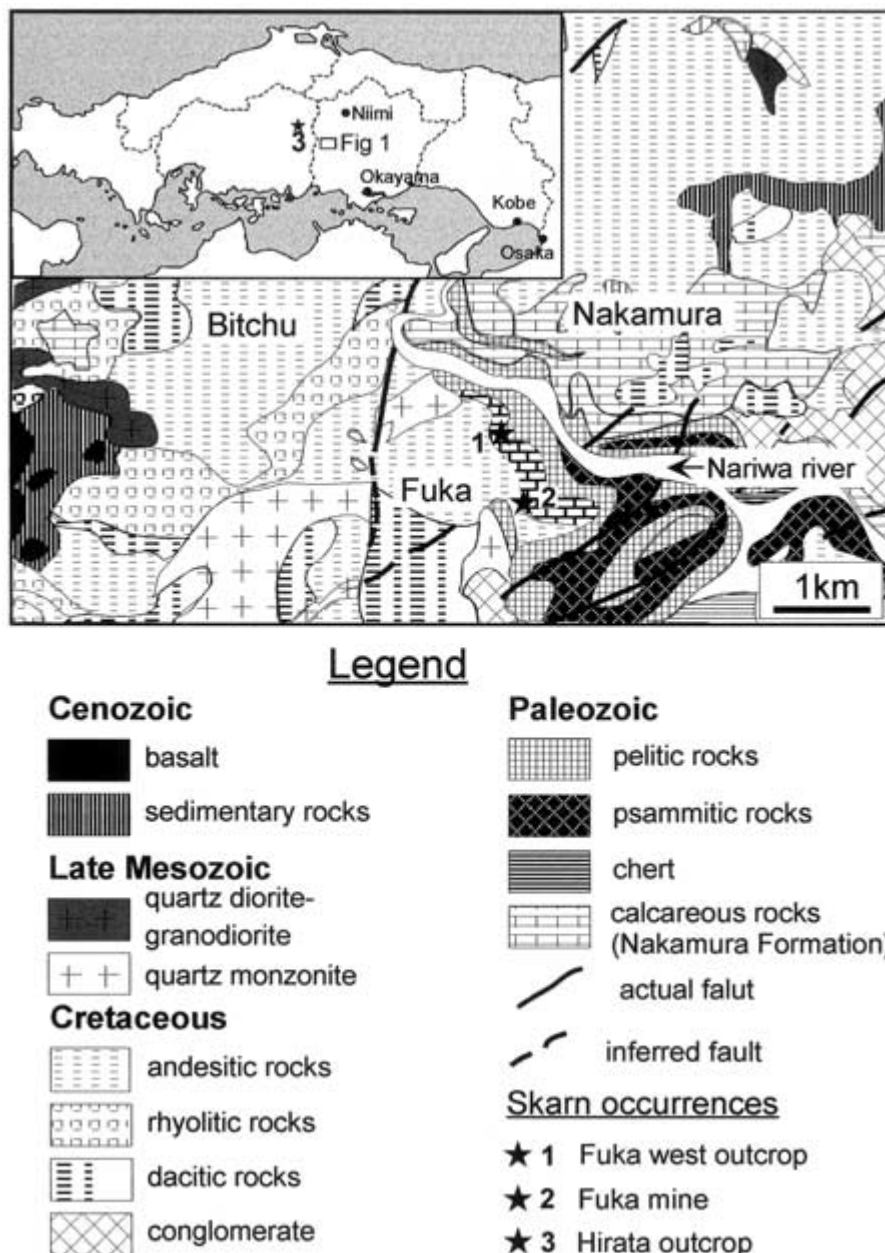


Fig. 1 Geological map of Fuka region showing the sampling localities of high-temperature skarn formation (modified after Teraoka et al., 1996).

using electronic optics. The operating conditions used for observing different minerals vary depending on the strength of the luminescence. For example, calcite which shows strong luminescence needs a low beam current ($\sim 1\text{mA}$), whereas silicate minerals which are less luminescent needs higher beam current (~ 1.5 to 2mA). The CL images in the present study were obtained using a beam current of $\sim 1.5\text{mA}$. Caution has to be taken not to expose the thin sections continuously with high beam current for long intervals, which will result in an increase in surface temperature and damage the thin section. If necessary, polished wafers should be used for observation, in-

stead of thin sections. Although the luminescence of some silicate minerals are not clearly visible using naked eye, photographs taken using long exposure time (up to 1 minute) display clear difference in luminescence between different mineral phases. Digital images presented in this study were filtered using the auto levels correction of Adobe Photoshop® software.

Sample descriptions and general geology

General geology

Two high-temperature skarn samples from Fuka, located about 40 km west-northwest of Okayama, and

one sample from Kushiro, Hiroshima Prefecture, southwest Japan, with contrasting mineral assemblages were selected for CL observations. The details of skarn formation at Fuka are given in Kusachi (1975), Omae *et al.* (2002) and Satish-Kumar *et al.* (2004) and a brief description is presented here. The basement rocks of Paleozoic age in this area comprise of sedimentary rocks of pelitic and psammitic composition, overlain by calcareous rock of the Nakamura Formation (Fig. 1). Volcanic rocks of Mesozoic age overly the sedimentary rocks in the western part of the Fuka region. Several generations of andesitic dikes intrude the basement rocks. Most of these dikes have 2-5 centimeter thick grossular - vesuvianite - wollastonite skarn of constant thickness parallel to the igneous-marble contact, indicating limited fluid activity and mass transport. However, extensive meter-scale high-temperature skarn formation surrounding monzodiorite/quartz monzonite intrusion is observed at Fuka, which display a zonal sequence consisting of gehlenite exoskarn - transition zone - spurrite endoskarn. A typical example of skarn occurrence is found in the Fuka North outcrop (Omae *et al.*, 2002). Here, the skarn formation is linked with two stages of igneous intrusion. The main high-temperature metasomatic gehlenite-spurrite skarn assemblage was formed as a result of the monzodiorite intrusion. Brief description of skarn outcrops from which samples were collected for CL microscopy is given below.

Wollastonite-grossular endoskarn at Fuka mine (Sample 0109132FST6-2)

Fuka mine is located in the south bank of Nariwa river (locality 1 in Fig. 1). Here, extensive mining of highly crystalline pure limestone has been carried out toward the igneous contact in four tunneling levels penetrating the hill. Inside the mine the retaining pillars and quarry faces preserve fresh outcrops of skarn. Generally, the skarn formation inside the mine comprises of spurrite or its alteration products, surrounding monzodiorite. The spurrite skarn is separated from the igneous intrusion by about 3-5 cm thick grossular-wollastonite endoskarn. The sample selected for CL studies is a grossular-wollastonite endoskarn from the second level of the mine.

Spurrite-tilleyite-gehlenite exoskarn at Fuka west outcrop (Sample 000916FKW1-2)

This outcrop is located at the western extremity of the contact metamorphic zone in Fuka (locality 2 in Fig. 1). Here, the skarn crops out at the slope of a hill. The skarn develop a zonal pattern, initiating from the quartz monzonite to thin wollastonite-grossular

endoskarn, through an intermediate thick gehlenite exoskarn and an outer spurrite-exoskarn. A transition zone can be observed between gehlenite and spurrite exoskarns (Kusachi *et al.*, 1978). Unaltered spurrite exoskarn is purple to grey in color. Patches and streaks (few centimeters in dimensions) of gehlenite occur within the monomineralic spurrite exoskarn. Hydrothermal alteration of spurrite is observed in the contact between the spurrite exoskarn and the host marble. The sample selected for CL studies was a typical purple colored spurrite-exoskarn.

Gehlenite-wollastonite exoskarn at Hirata outcrop, Kushiro, Hiroshima (Sample 000917ST4-3)

High-temperature gehlenite-wollastonite exoskarn is exposed in this locality (Fig. 1; inset). Contrasting to the occurrence in Fuka outcrops, the Hirata outcrop has extensive gehlenite exoskarn. However, most of the gehlenite is retrogressed to form hydrogrossular or vesuvianite. A typical gehlenite exoskarn sample was selected for CL studies.

Cathodoluminescence observations

Sample 0109132FST6-2

This sample is characterized by fine grained intergrowth of wollastonite and grossular (Plate 1-a). Scaly wollastonite shows purple blue luminescence in the core portions with yellow CL in the rim. Bright bluish-pink luminescence can be noticed along a fracture zone in the wollastonite-rich zone (Plate 1-b).

Sample 000916FKW1-2

Spurrite and tilleyite dominate this sample. However, both minerals have similar optical properties under open and crossed polarized light (Plate 1-c). CL image of spurrite and tilleyite is shown plate 1d. Spurrite shows characteristic green luminescence whereas pink luminescence is characteristic of tilleyite, similar to those reported from Kilchoan (Long & Agrell, 1965). Plate 2-a and 2-c shows aggregates of rankinite under crossed polarized light. However, CL images shows bright red luminescence for rankinite and zones with yellow CL, which is kilchoanite, the low temperature polymorph of rankinite (Plates 2-b, -d). Because of the high luminescence of rankinite, spurrite and tilleyite are difficult to identify in the CL image.

Sample 000917ST4-3

Plate 3 shows typical high-temperature wollastonite associated with hydrogrossular (Plate 3-a) formed by the retrogression of gehlenite. In the CL image, two specific CL zones can be noticed within a sin-

Table 1 Representative chemical composition of high-temperature skarn minerals that exhibit cathodoluminescence.

Mineral	garnet	garnet	Wollastonite	Wollastonite	Rankinite	Rankinite	Spurrite	Spurrite	Tilleyite	Tilleyite	Wollastonite	Wollastonite
Analysis No.	0109132FST 6-2-182	0109132FST 6-2-185	0109132FST 6-2-16	0109132FST 6-2-17	0916FKW1- 2-1-90	0916FKW1- 2-1-91	0916FKW1- 2-26	0916FKW1- 2-27	0916FKW1- 2-20	0916FKW1- 2-21	000917ST4- 3-30	000917ST4- 3-22
CL colour	No	No	Purple	Yellow	Orange red	Yellowish orange	Green	Green	Pink	Pink	Purple	Yellow
SiO ₂	36.51	37.08	50.52	50.60	39.96	40.73	26.54	26.56	24.56	24.06	51.33	50.66
TiO ₂	1.67	1.31	0.40	0.38	0.30	0.30	0.29	0.31	0.26	0.31	0.39	0.32
Al ₂ O ₃	12.28	12.41	0.27	0.25	0.27	0.11	0.14	0.13	0.10	0.11	0.25	0.29
Cr ₂ O ₃	0.14	0.14	0.12	0.12	0.12	0.12	0.13	0.11	0.10	0.16	0.16	0.15
FeO	12.81	12.79	0.22	0.26	0.26	0.28	0.23	0.24	0.22	0.21	0.28	0.26
MnO	0.23	0.20	0.15	0.16	0.22	0.17	0.19	0.16	0.16	0.11	0.21	0.19
MgO	0.37	0.25	0.14	0.11	0.15	0.13	0.13	0.13	0.12	0.14	0.22	0.19
CaO	35.53	35.71	48.43	48.50	55.62	57.49	60.51	60.68	55.93	56.29	48.30	48.49
Na ₂ O	0.09	0.09	0.11	0.10	0.11	0.10	0.19	0.28	0.11	0.09	0.11	0.15
K ₂ O	0.10	0.09	0.11	0.11	0.09	0.11	0.13	0.15	0.08	0.09	0.10	0.12
Total	99.72	100.06	100.46	100.59	97.73	100.19	89.09	89.37	82.25	82.16	101.35	100.81
Cations on the basis of	12 (O)	12 (O)	3 (O)	3 (O)	7 (O)	7 (O)	9 (O)	9 (O)	9 (O)	9 (O)	3 (O)	3 (O)
Si	2.979	3.009	0.979	0.979	1.979	1.972	1.998	1.995	2.002	1.971	0.984	0.978
Ti	0.102	0.080	0.006	0.006	0.011	0.011	0.016	0.017	0.016	0.019	0.006	0.005
Al	1.181	1.187	0.006	0.006	0.016	0.006	0.012	0.011	0.009	0.010	0.006	0.007
Cr	0.009	0.009	0.002	0.002	0.005	0.005	0.008	0.006	0.007	0.010	0.002	0.002
Fe	0.874	0.868	0.004	0.004	0.011	0.011	0.015	0.015	0.015	0.014	0.004	0.004
Mn	0.016	0.014	0.002	0.003	0.009	0.007	0.012	0.010	0.011	0.008	0.003	0.003
M	0.045	0.030	0.004	0.003	0.011	0.009	0.014	0.014	0.015	0.017	0.006	0.005
Ca	3.106	3.105	1.005	1.006	2.951	2.982	4.881	4.882	4.885	4.940	0.992	1.004
Na	0.014	0.014	0.004	0.004	0.010	0.010	0.028	0.040	0.017	0.013	0.004	0.005
K	0.010	0.010	0.003	0.003	0.006	0.006	0.012	0.015	0.009	0.010	0.002	0.003
Total	8.336	8.325	2.015	2.014	5.008	5.020	6.996	7.006	6.986	7.012	2.010	2.017

gle crystal of wollastonite: 1) blue CL in the core showing sector zoning (Plate 3-b) and 2) yellow CL portion in the rim (Plate 3-c) or along cleavage planes (Plate 3-d). Hydrogrossular and gehlenite in this sample do not generate luminescence.

Mineral chemistry

Representative mineral chemical compositions of garnet, wollastonite, rankinite spurrite and tilleyite were measured using an electron probe microanalyzer (JEOL-JCXA733) at the Centre for Instrumental Analysis, Shizuoka University. Corrections were made according to Bence and Albee (1968) using factors of Nakamura & Kushiro (1970). Accelerating voltage was 15 kV and beam current was 1.2×10^{-8} A. Representative results are given in Table 1. Major element chemical composition of skarn minerals are comparable with those reported in Deer *et al.* (1992) as well as those reported from similar skarn occurrence in Apuseni Mountains, Romania (Pascal *et al.*, 2001; Marincea *et al.*, 2001). Irrespective of variations in luminescence within single grains, appreciable major element compositional variations could not be detected.

Conclusions

There are several advantages in using CL microscopy. In the present study, we could use the CL images to distinguish optically similar minerals such as

spurrite and tilleyite. Rankinite and kilchoanite were also easily distinguished using the CL images. CL images were also useful in the identification of micrometer size mineral inclusions. Most important application of CL image was the identification of growth and alteration textures in wollastonite and rankinite. Crystal growth zones were easily identified using CL images. The growth zones within single crystals may indicate the changing skarn formation conditions, possibly resulting from varying trace element and REE contents. Variations in CL are related to the molecular distortions within the crystal lattice, such as impurity atoms or lattice defects (Marshall, 1988). Some impurity atoms act as activators and enhance luminescence, while others act as quenchers and suppress the luminescence (Yardley & Lloyd, 1989). Earlier studies have identified the correlative distribution of trace elements with the varying CL colour and brightness (Pagel *et al.*, 2000). For example, CL observations in calcite and dolomite recognized Mn^{2+} as an activator and Fe^{2+} as quencher (Long & Agrell, 1965). In the present study, although we could observe CL variations within single wollastonite grains, it was unable to link it with chemical variations. Further detail trace element study is necessary to understand the CL variations in minerals.

In summary, CL microscopy is an easy, useful and non-destructive technique to observe the chemical heterogeneity in natural samples.

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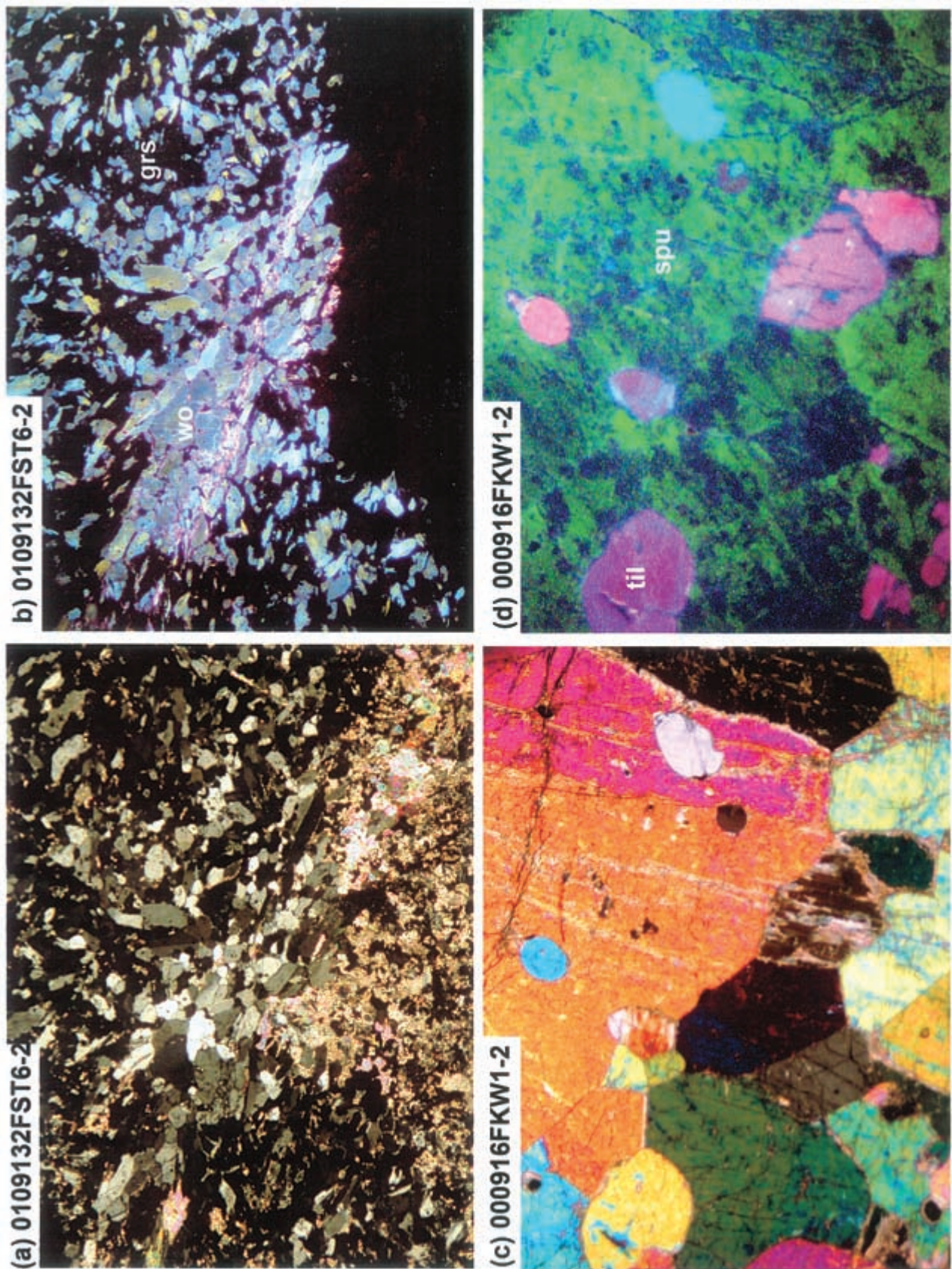


Plate 1 Photomicrographs of selected skarn minerals from Fuka, Okayama, Japan (width of the photomicrographs is ~ 2 mm).

Mineral abbreviations; grs - grossular garnet; spu - spurrite; til - tilleyite; wo - wollastonite.

(a) Fine grained intergrowth of wollastonite+grossular endoskarn in crossed polarized light at the contact between igneous rock and exoskarn.

(b) Yellow to purple cathodoluminescence of wollastonite.

(c) Coarse grained spurrite+tilleyite exoskarn (crossed polarized light).

(d) Spurrite and tilleyite shows typical green and pink cathodoluminescence, respectively.

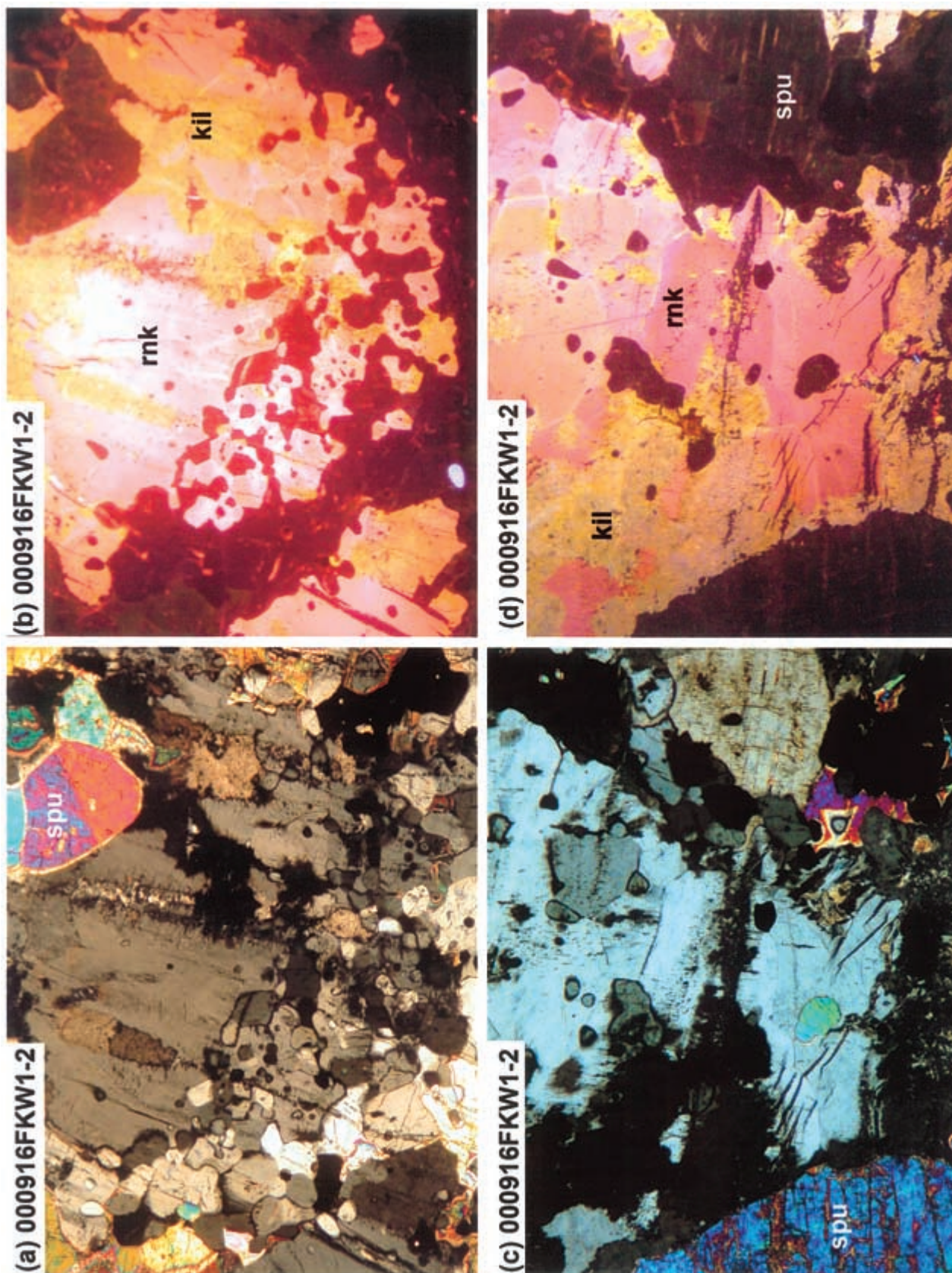


Plate 2 Photomicrographs of selected skarn minerals from Fuka, Okayama, Japan (width of the photomicrographs is ~ 2 mm).

Mineral abbreviations; kil - kilchoanite; spu - spurrite; rnk - rankinite.

- (a) Rankinite aggregate showing altered zones under crossed polarized light.
- (b) Pinkish red CL of rankinite and yellowish orange zones of kilchoanite.
- (c) Rankinite in association with spurrite under crossed polarized light.
- (d) Pinkish red CL of rankinite and yellowish orange zones of kilchoanite.

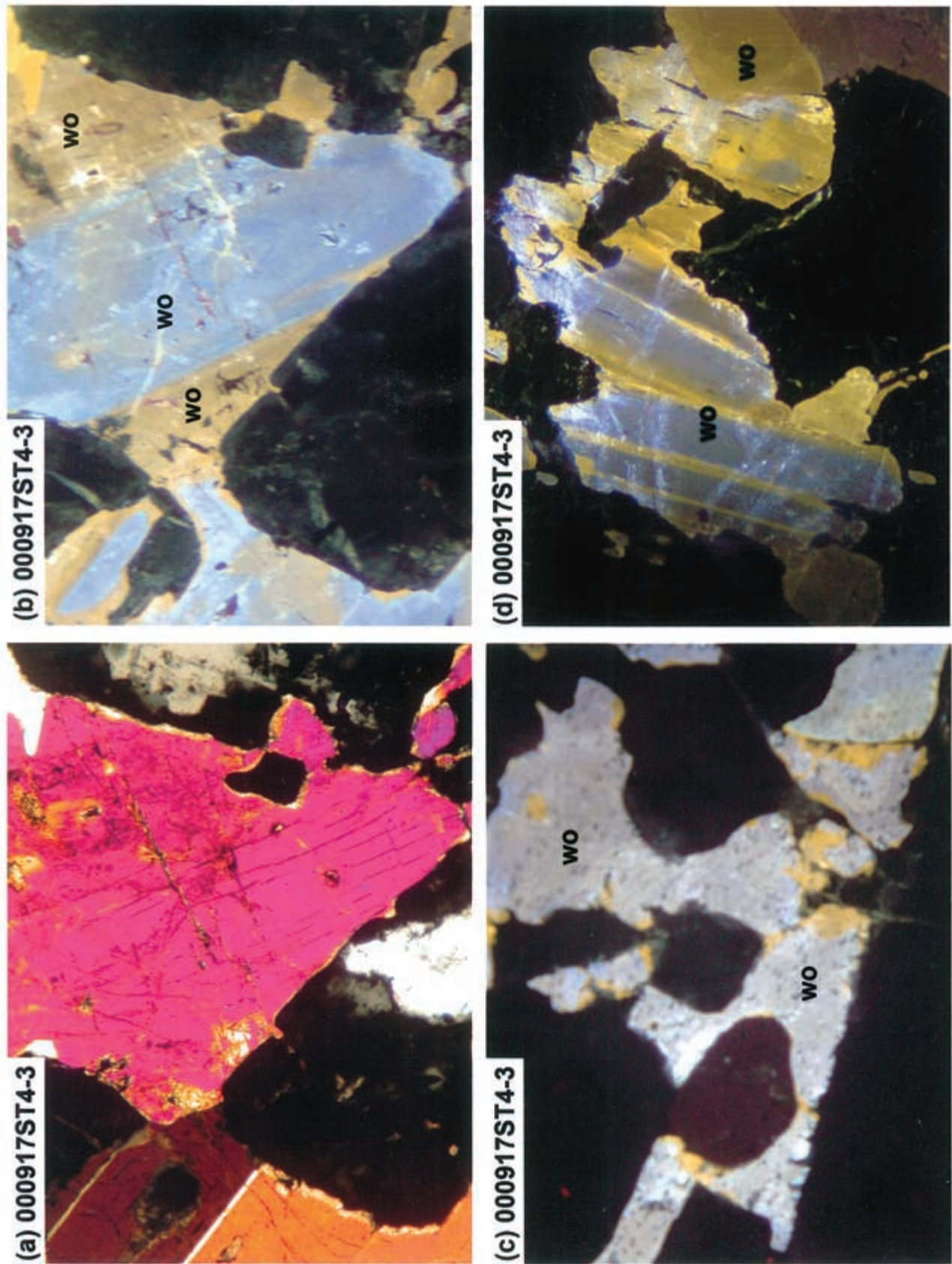


Plate 3 Photomicrographs of selected skarn minerals from Fuka, Okayama, Japan (width of the photomicrographs is ~ 2 mm).

Mineral abbreviation; wo - wollastonite.

- (a) Interstitial single grain of wollastonite within hydrogrossular pseudomorphs after gehlenite under crossed polarized light.
- (b) CL image of wollastonite showing distinct purple core and yellow rim. Note the purple core portion shows growth zones.
- (c) CL image of interstitial wollastonite with thin rims of yellow CL portions.
- (d) Cleavage parallel domains showing contrasting CL colors within a single wollastonite crystal associated with hydrogrossular.