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CORUNDUM+QUARTZ ASSOCIATION IN ARCHEAN GRANULITE-FACIES ROCK FROM ENDERBY LAND, EAST ANTARCTICA: PRELIMINARY INTERPRETATION

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Abstract: Corundum occurs in direct contact with quartz in a high-temperature granulite-facies metamorphosed quartzite from the Archean Napier Complex in Enderby Land, East Antarctica. The quartzite is composed dominantly of bluish-gray quartz with mesoperthitic K-feldspar and spinel as subordinate constituents. Corundum occurs always being interlocked with spinel and both minerals are in direct contact with quartz. Under the *P-T* conditions of the Napier granulites (900–1000°C, 7–10 kbar), sillimanite should be a stable Al_2SiO_5, and corundum cannot coexist stably with quartz. On the basis of the petrographical evidence, the corundum is inferred to be an exsolved product from spinel solid solution upon cooling, and it did not react with surrounding quartz to form Al_2SiO_5 probably due to the high activation energy required for the solid-solid interaction between corundum and quartz.

1. Introduction

Natural association** of corundum+quartz was found in the metamorphosed quartzite (specimen no. AM-Y-08) collected at Mt. Riiser-Larsen (66°47′S latitude, 50°42′E longitude) in Enderby Land, East Antarctica. This area is geologically referred to as the Napier Complex which is underlain by the Archean granulite-facies rocks with unique mineral assemblages including sapphirine+quartz, orthopyroxene+sillimanite+quartz, spinel+quartz and osumilite in meta-pelitic or meta-quartzofeldspathic rocks (SHERATON *et al.*, 1980; ELLIS *et al.*, 1980; GREW, 1980; MOTOYOSHI and MATSUEDA, 1984). The physical conditions of the peak of metamorphism were probably beyond the stability of garnet-cordierite coexistence and the *P-T* estimates are in the range of 900–1000°C and 7–10 kbar (SHERATON *et al.*, 1980; ELLIS *et al.*, 1980; ELLIS, 1980; GREW, 1980; MOTOYOSHI and MATSUEDA, 1984; HARLEY, 1985, 1987; SANDIFORD and WILSON, 1983, 1984; SANDIFORD, 1985; SANDIFORD and POWELL, 1986). Moreover, P_{H_2O} must have been much lower than P_{Total} because of absence of mig-

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** The term "association" in this paper is used to suggest a group of minerals in small areas of a sample, but the minerals are not necessarily in equilibrium with each other.

matite in spite of the high *P-T* conditions, and of presence of calcic mesoperthite (SHERATON *et al.*, 1980).

This paper gives a preliminary interpretation of the association of corundum+quartz in natural granulite-facies environment under which sillimanite was a stable Al_2SiO_5 mineral.

2. Petrography and Mineral Chemistry

Metamorphosed quartzite in question (specimen no. AM-Y-08) is a member of the Napier granulites and is considered to have been subjected to the high-temperature metamorphism as stated above. This rock is composed dominantly of bluish-gray quartz with mesoperthitic K-feldspar and spinel as subordinate constituents and zircon as an accessory. Corundum, sapphirine, ilmenite and rutile are all interlocked with spinel. In addition to these minerals, orthopyroxene and unidentified Al-Fe-Mg-K hydrated silicate, which are also associated with spinel, are recognized by the scanning electron microscope with an energy dispersive analyzer. Mineral analyses in this paper were all performed by an electron microprobe analyzer using JEOL JCXA-733 at the National Institute of Polar Research. Specimen current was kept at 0.012–0.015 microampere and accerelating voltage at 15 kV. Synthesized pure oxides and natural minerals were used for standards with intensity data being adjusted to BENCE

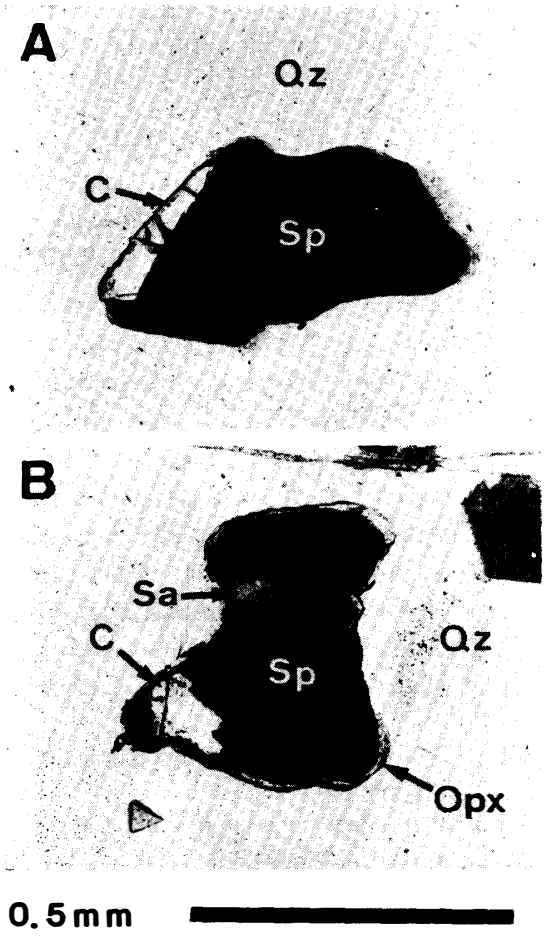

Fig. 1. Photomicrographs showing the mode of occurrence of corundum (C), quartz (Qz), spinel (Sp), sapphirine (Sa) and orthopyroxene (Opx) in the metamorphosed quartzite (specimen no. AM-Y-08). A: Corundum in association with spinel and surrounding quartz. Note that no reaction products are observed between corundum and quartz. B: Association of corundum, sapphirine, spinel and surrounding quartz. Thin film armouring spinel is orthopyroxene.

Table 1. Representative microprobe analyses of corundum, quartz, spinel, sapphirine and ilmenite in the metamorphosed quartzite (specimen no. AM-Y-08).

	Corundum	Quartz	Spinel	Sapphirine	Ilmenite
SiO_2	0.01	98.93	—	11.24	0.13
TiO_2	0.01	0.10	0.01	0.04	51.48
Al_2O_3	98.54	0.28	58.79	64.32	0.13
Cr_2O_3	0.41	0.11	2.12	0.62	0.06
Fe_2O_3*	0.61	—	—	—	—
FeO	—	0.05	28.76	7.48	46.01
MnO	0.07	—	0.01	0.02	0.31
MgO	—	—	9.55	14.81	0.90
CaO	0.03	—	0.01	—	—
NiO	0.03	0.03	0.27	0.12	—
ZnO	—	—	0.18	—	—
Total	99.71	99.50	99.70	98.65	99.02
O	3	2	4	20	6
Si	0.000	0.996	—	1.360	0.007
Ti	0.000	0.001	0.000	0.003	1.957
Al	1.985	0.003	1.913	9.173	0.008
Cr	0.006	0.001	0.048	0.059	0.002
Fe^{3+}**	0.008	—	0.028	0.047	0.063
Fe^{2+}	—	0.000	0.605	0.710	1.883
Mn	0.001	—	0.004	0.002	0.013
Mg	—	—	0.398	2.672	0.068
Ca	0.001	—	0.000	—	—
Ni	0.000	0.000	0.006	0.011	—
Zn	—	—	0.005	—	—
$Mg/(Fe^{2+}+Mg)$	—	—	0.397	0.790	—
Fe^{3+}/Fe^{2+}	—	—	0.046	0.066	0.033

* Total Fe as Fe_2O_3 for corundum and FeO for other minerals.

** Fe^{3+} is calculated assuming $(Si+Ti+Al+Cr+Fe^{3+})=2.000$ for spinel, after HIGGINS *et al.* (1979) for sapphirine and after CARMICHAEL (1967) for ilmenite, respectively.

and ALBEE's (1968) correction method. Representative analyses of the minerals are listed in Table 1.

Corundum: It is noteworthy that corundum occurs always being interlocked with spinel, *i.e.* it fringes spinel rim, or it occurs as blebs in spinel (Fig. 1). An important fact is that corundum is in direct contact with quartz and any reaction products are not observed between them under the optical microscope. This observation was further confirmed by the backscattered electron image of the scanning electron microscope in a small scale along the corundum-quartz contact. Corundum contains iron and chromium up to 0.61 wt% Fe_2O_3 and 0.41 wt% Cr_2O_3.

Quartz: Quartz predominates, being over 90% in modal proportion, in the rock. It shows microscopically complicated wavy extinction and includes unidentified tiny grains and needles. The grain boundary generally shows a sutured-like structure. Microprobe analysis indicates the presence of impurities in small amounts as presented in Table 1.

Spinel: Spinel occurs sporadically as independent grains, and it is occasionally

idiomorphic being ordinarily in direct contact with surrounding quartz (Fig. 1). However, in places, secondary alteration product is observed along spinel rim, or in other cases orthopyroxene armours spinel (Fig. 1B). Spinel approximately corresponds to hercynite-spinel solid solution with some Cr_2O_3 at around 2 wt%. The ZnO content is always less than 0.5 wt%, and the effect of Zn to stabilize it in the presence of quartz would be negligible. Recalculated values of Fe^{3+} from stoichiometry are considerably low at around $Fe^{3+}/Fe^{2+}=0.04$–0.07.

Sapphirine: Sapphirine is occasionally associated with spinel and corundum as shown in Fig. 1B, and is also in direct contact with quartz. Its chemical composition indicates that it has $Mg/(Fe^{2+}+Mg)=0.79$ and low Fe^{3+}/Fe^{2+} ratio at around 0.07.

Ilmenite: Ilmenite is rarely observed to be associated with spinel and corundum. It is microscopically homogeneous free from exolution lamellae under the reflected light, which is also suggested by the low Fe^{3+}/Fe^{2+} at 0.03.

K-feldspar: Subordinate amount of K-feldspar is locally observed among quartz grains. It always shows a mesoperthitic texture.

3. Discussion

3.1. *Instability of corundum+quartz*

Stability of corundum+quartz may be assessed thermodynamically considering the hypothetical equilibrium, for example,

$$\text{corundum}+\text{quartz}=\text{sillimanite}\ . \tag{1}$$

However, because the change in the free energy ($\Delta G_{\text{reaction}}$) of equilibrium (1) is only 1 kJ (BOHLEN *et al.*, 1986), which is well within the uncertainties of the thermochemical data for the phases, it is almost impossible to determine equilibrium (1) precisely only by thermodynamic calculation.

In relation to $\Delta G_{\text{reaction}}$ of equilibrium (1), BOHLEN (1986) performed experiments for

$$\text{hercynite}+\text{quartz}=\text{almandine}+\text{sillimanite}\ , \tag{2}$$

$$\text{hercynite}+\text{sillimanite}=\text{almandine}+\text{corundum}\ , \tag{3}$$

by means of the piston-cylinder apparatus. In order for corundum+quartz to coexist stably, it is necessary that equilibria (2) and (3) must intersect. Assuming ± 0.1 kbar and ± 5°C uncertainty, he assessed the minimum and maximum dP/dT of equilibrium (2) to be 23–28 bar/°C, and of equilibrium (3) to be 17–24 bar/°C, respectively. The results imply that the possible intersection of the equilibria lies at above 1150°C and above 13 kbar, or they do not intersect. These data apparently suggest that corundum cannot coexist with quartz stably in the crustal environment even under the high-temperature conditions of the Napier granulites.

3.2. *Formation of corundum*

Corundum in AM-Y-08 is always interlocked with spinel and it seems to be an exsolved product from spinel judging from the mode of occurrence.

In the MgO-Al_2O_3 system, it is well known that extensive solid solution can be formed between $MgAl_2O_4$ and Al_2O_3 under the high temperatures based on the substitution $2Al^{3+}=3Mg^{2+}$. During the cooling of this spinel solid solution, it is expected that the solubility of Al_2O_3 in spinel decreases and excess Al_2O_3 would exsolve as corundum. This phenomenon has been experimentally observed in the field of ceramics (*e.g.* KINGERY *et al.*, 1976).

3.3. Interpretation of corundum+quartz in direct contact

Under the *P-T* conditions of the Napier granulites, sillimanite should be a stable Al_2SiO_5 and it occurs commonly in meta-pelitic rocks being associated with garnet, orthopyroxene, sapphirine, osumilite, etc., depending on the bulk chemical compositions. Therefore, a reasonable explanation is required for the association of corundum+quartz in direct contact.

One possible interpretation is that corundum exsolved from spinel under considerably lower temperatures than the peak metamorphic conditions as mentioned above, and the effective diffusion of elements did not occur to cause chemical reaction.

Another possibility is that nucleation of sillimanite by the solid-solid interaction between corundum and quartz requires a high activation energy even under the high-temperature condition of the Napier granulites.

Although we have not reached any definite conclusion, experimental, theoretical and crystallographic investigations would clarify the natural association of corundum+quartz in emeries and other high-grade meta-pelites (TRACY and MCLELLAN, 1985; BOHLEN, 1986).

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