

Geochemistry of plutonic spinels from the North Kamchatka Arc: comparisons with spinels from other tectonic settings

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Abstract

Ultramafic to mafic plutons in the Olyutor Range, North Kamchatka, represent the magmatic roots of a late Eocene arc, related to the westward subduction of the Komandorsky Basin beneath the Asian continental margin. Olyutor Range plutons are concentrically zoned with cumulate dunite cores mantled by a wehrlite-pyroxenite transitional zone and, in turn, by a narrow gabbroic rim.

Spinel is a common accessory mineral in these arc plutonics, and we present analyses of spinels from a range of lithologies. A continuous compositional trend is observed from Cr-spinel in the ultramafics to Cr-rich magnetite in marginal gabbros. Complex chemical zoning patterns within individual spinel grains suggest an interplay between fO_2 , fractionation, volatile content and subsequent sub-solidus re-equilibration of spinel with co-existing silicates (mainly olivine).

In general, the spinels from magmatic arc environments are characterised by high total Fe and high Fe^{3+} contents compared to MORB and boninitic spinels and higher Cr-values relative to oceanic basin spinels. These differences imply a high oxygen fugacity during arc petrogenesis. Differences are also observed between plutonic spinels from arcs and low-Ti supra-subduction zone ophiolites. Low-Ti ophiolitic spinels are generally poorer in iron and richer in Cr, and hence are similar in composition and perhaps tectonic setting to fore-arc boninitic spinels.

KEYWORDS: spinel, ultramafic, mafic, pluton, Kamchatka, geochemistry.

Introduction

SPINELS are recognised as important petrogenetic indicators (Irvine, 1967; Dick and Bullen, 1984) and can be used to investigate the conditions of magma evolution and emplacement of plutonic bodies (Agata, 1988; Jan and Windley, 1990). The plutons of North Kamchatka represent the exposed plumbing system of the Eocene magmatic arc (Reuber *et al.*, 1991). As spinels are a common accessory phase in these plutonics, it provides an opportunity to characterise the

chemistry of spinels from a calc-alkaline arc environment. This enables these arc spinels to be compared with examples from other tectonic settings and provide a more comprehensive basis for discrimination of original tectonic environments in plutonics of uncertain origin.

Geochemical and petrological studies of many ophiolite complexes have revealed a complicated tectonic setting and support their formation in supra-subduction zones rather than oceanic ridge environments (Pearce *et al.*, 1984; Stern *et al.*, 1989; Taylor *et al.*, 1992*b*). This suggestion is consistent with a lack of typical MORB-type basalts in ophiolites and a widespread association of boninites with arc tholeiites in ophiolite dyke

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units and lava sequences (Cameron, 1985; Flower and Levine, 1987; Beccaluva and Serri, 1988). Furthermore, comparison of representative geochemical transects in well-documented ophiolites (e.g., Troodos) with arc-fore-arc basin sequences (Marianas, Izu-Bonin) revealed their close similarity, suggesting derivation of some ophiolite fragments from the back-arc basin-island arc-fore-arc complexes (Hawkins *et al.*, 1984).

The petrology and geochemistry of supra-subduction zone (SSZ) ophiolite plutonic complexes seem to be different from those of the exposed arc-related plutonic complexes (Snoké *et al.*, 1981). Structural studies of arc plutons also suggest different conditions of crystal accumulation and chemical convection which imply the different processes operating in ophiolite and arc-related magma chambers (Nicolas *et al.*, 1988).

We report in this paper the results of the study of zoned spinels in ultramafic to mafic plutons from the North Kamchatka arc.

Geologic setting of the arc plutonism in North Kamchatka

The North Kamchatka region is the southernmost extension of the Koryak Foldbelt and is composed of oceanic and island arc-derived terranes of Cretaceous to Paleogene age which were accreted to the Eurasian continental margin during the Late Cretaceous to Middle Eocene (Bogdanov *et al.*, 1987; Bogdanov and Fedorchuk, 1987) (Fig. 1). The North Kamchatka magmatic arc was associated with a westward subduction of the young crust of the Paleo-Komandorsky Basin generated around 45 Ma as suggested by micropaleontological evidence from the arc volcanic-sedimentary sequence (Chekhovich *et al.*, 1990) and geochronology of arc plutons (Firsov, 1987; Kepezhinskias *et al.*, in press). The initiation of subduction along the Kamchatka active margin is dated by 45 Ma-old arc tholeiite sequences in the southern segment of the arc and 44–47 Ma shoshonite dykes and differentiated calc-alkaline plutonic bodies in the northern segment of the arc (Aprel'kov *et al.*, 1991; Fedorchuk and Izvekova, in press). Subduction was most likely initiated along a transform fault plate boundary (Bogdanov and Fedorchuk, 1987; Bogdanov *et al.*, 1987).

The Olyutor Range is located in the northeastern part of the arc (Fig. 1). It comprises various oceanic and island arc-type volcanic-sedimentary complexes which are overthrust northwestwards onto the Late Cretaceous-Paleogene Koryak flysch (Fig. 2). The accreted ter-

ranes are intruded by numerous ultramafic to intermediate zoned plutons associated with calc-alkaline basalt and basaltic andesite dykes and lavas (Fig. 2 and 3). The magmatic arc is built on top of the accreted oceanic crust with angular unconformity between Cretaceous oceanic and Late Eocene island arc sequences. The K–Ar dating of hornblende, phlogopite, K-feldspar and plagioclase separates from the Olyutor range plutons, yielded ages around 45–48 Ma (Kepezhinskias *et al.*, in press). All ultramafic and mafic to intermediate plutons from the North Kamchatka arc plot along calc-alkaline trends on AFM and Ca–Na–K diagrams (Fig. 4) which is consistent with their magmatic emplacement in an island arc setting.

Petrography and field relations of the plutons

Two major pluton types can be recognised in the Olyutor Range: Epilchik-type (E-type) plutons with dunite core, wehrlite-pyroxenite transitional zone and a thin gabbroic rim and Machevna-type (M-type) composite plutons with felsic (diorites, granodiorites, tonalites) cores and gabbroic rims containing lenses of ultramafic cumulates (Reuber *et al.*, 1991; Kepezhinskias *et al.*, in press). Spinel is mainly developed in the ultramafic core of the E-type plutons which, consequently, are the major focus of this paper.

The E-type plutons exhibit a concentric structure with a dunitic core intruded by numerous cross-cutting pyroxenitic dykes, followed by a wehrlite-pyroxenite transitional zone and a discontinuous gabbroic margin commonly 50 to 100 m in thickness (Fig. 3). The grain size of the marginal gabbros progressively decreases towards the contact due to the effect of chilling.

Petrography of the E-type plutons is described in detail by Reuber *et al.* (1991) and Kepezhinskias *et al.*, (in press), and only a brief summary is given here. Massive core dunites are characterised by fresh olivine up to 1 mm in size, about 3% modal spinel and trace amounts of intercumulus clinopyroxene. Clinopyroxenites are composed mainly of relatively large crystals (up to 10 mm) of diopside with variable, but usually small, amounts of olivine, amphibole and phlogopite. Wehrlites display poikilitic textures with 15 mm oikocrysts of clinopyroxene containing inclusions of fine- to medium-grained olivine. Marginal gabbros are fine- to medium-grained and commonly show coarse sub-ophitic textures. They contain clinopyroxene and plagioclase with variable amounts of olivine, amphibole, phlogopite and Fe-Ti oxides.

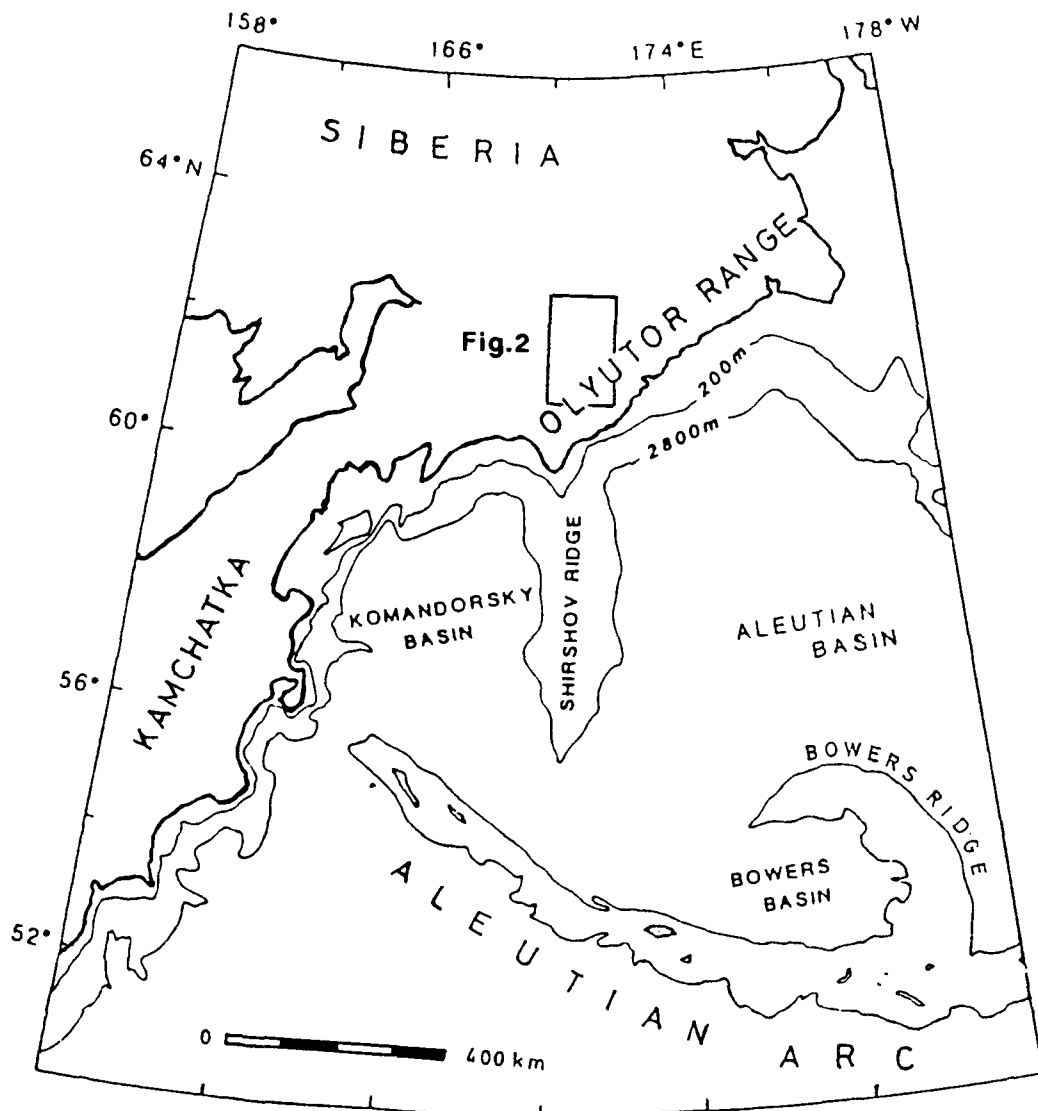


FIG. 1. Index map of the North Kamchatka and adjacent areas. The location of Fig. 2 is shown by the box.

Occurrence of spinels

Spinel commonly forms octahedral to round crystals with sizes varying from 0.2 to 0.8 mm. It is also observed as an inclusion in phenocrystal olivine from the clinopyroxene-free dunites and in this case it displays typical octahedral shape. Magmatically disaggregated spinels occur in dunites located along the vertical magmatic flow planes within the E-type cores.

In wehrlites from the transitional zone, spinel is commonly associated with layered wehrlite-pyroxenite-olivine-rich wehrlite sequence. It is

observed as equant inclusions in olivine and, rarely, as relatively large (up to 1 mm) anhedral crystals intergrowing with olivine and clinopyroxene. In several samples from the dunite core of the West Epilchik pluton, clinopyroxene is replacing spinel probably due to pressure-dependent reaction along the pyroxene-olivine cotectic line (Fisk and Bence, 1980; Jan and Windley, 1990).

Mineral chemistry

Mineral chemistry of ultramafic and mafic rocks from the E-type plutons are discussed in detail in

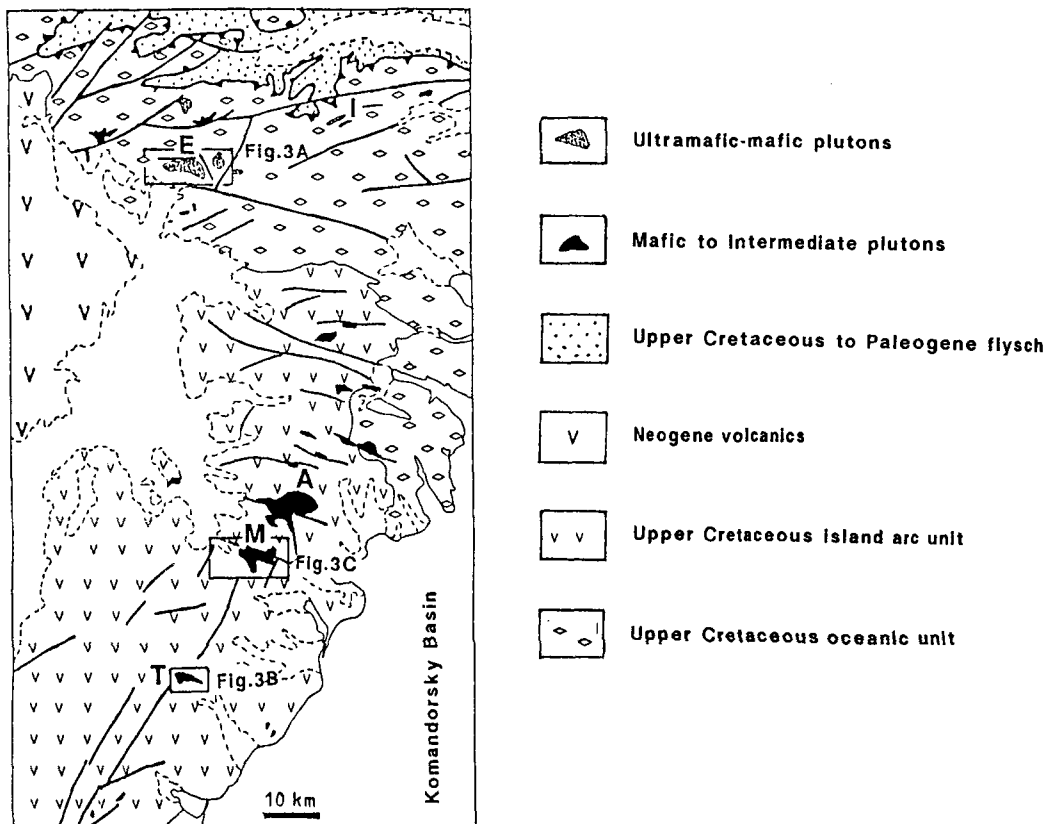


Fig. 2. Geological setting of arc-related plutons in the Olyutor Range, North Kamchatka. E—Epilchik group, M—Machevna group, T—Tigil pluton. Location of geological maps of individual plutons is shown by boxes.

several papers (Reuber *et al.*, 1991; Kepezhinskas and Savichev, 1991; Tanaka *et al.*, 1992; Kepezhinskas *et al.*, in press). Here a brief summary of silicate mineralogy is provided followed by a more detailed examination of spinel chemistry. Mineral analyses of the spinels were performed using the CAMEBAX electron microprobe at the Institute of Geology and Geophysics (Novosibirsk, Russia). Operating conditions were: a 20 kV accelerating voltage, a probe current of 14 nA, a counting time of 10 sec. per element, and a beam diameter of approximately 2 μm . A set of natural and synthetic standards was used and the data were processed following the ZAF-corrections procedure of Bence and Albee (1968) modified by Albee and Ray (1970).

Olivine. Olivine compositions are relatively uniform in dunites from the E-type plutonic cores (Fig. 5). Fo contents lie in the range 87.8 to 89.0 for West Epilchik dunites, and 88.2 to 89.1 for East Epilchik dunites. In comparison, olivines from wehrlites are more Fe-rich, which is consistent with the crystallisation of wehrlites (and

pyroxenites) from more evolved liquid. Olivines from the West Epilchik transitional zone wehrlites range between Fo 82.0 and Fo 86.2, while in East Epilchik the olivines have a more restricted compositional range (Fo 80.3–82.2).

Clinopyroxene. Ca-rich pyroxenes from E- and M-type plutons are classified as diopsides and plot as a compact field on a pyroxene quadrilateral (Fig. 5). Clinopyroxene oikocrysts in dunites have Cr-contents in the range 0.51–0.90 wt.% Cr_2O_3 at high Mg# (88–91). Diopsides from the transitional zone ultramafics are less MgO-rich (Mg# 83–88) and correspondingly Cr-poor (0.20–0.45 wt.% Cr_2O_3). These differences in pyroxene chemistry parallel the changes in olivines between dunite core and wehrlite-pyroxenite transitional zone.

Orthopyroxene. Rare orthopyroxene oikocrysts are found in transitional zone wehrlites from the West Epilchik pluton. They are commonly low-Al bronzites with low-Cr and low-Ni contents.

Amphibole. High-Mg amphibole forms an-

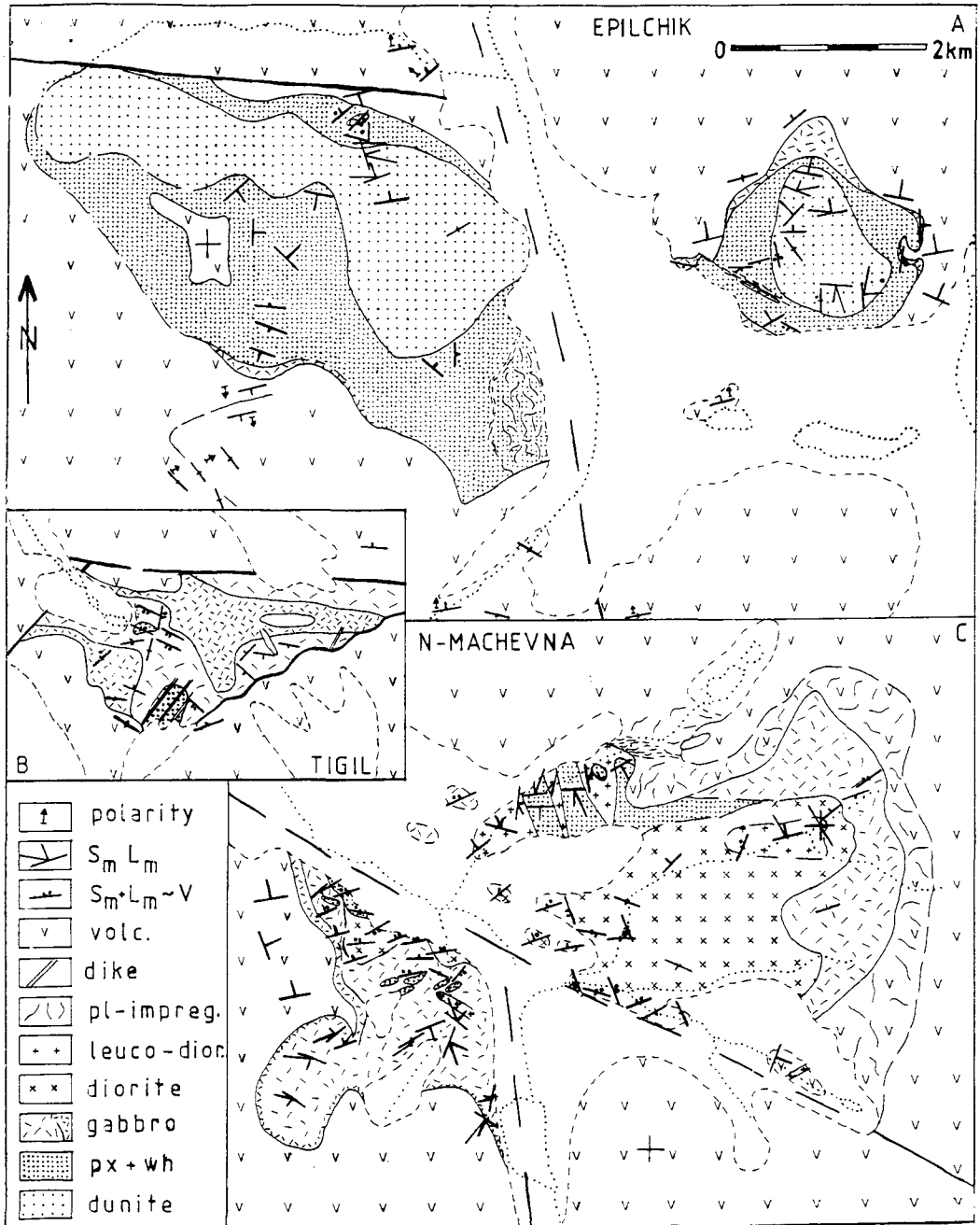


FIG. 3. Detailed geologic maps of representative plutons: (A) West and East Epilchik (E-type), (B) Tigil (M-type), and (C) Machevna (M-type).

hedral crystals along the inter-grain boundaries in some dunites from the East Epilchik pluton and replaces clinopyroxene in ultramafic rocks from the east part of the West Epilchik massif.

Replacement was probably produced through reaction with clinopyroxene during percolation of H_2O -rich residual felsic liquid through the wehrlite-pyroxenite transitional zone.

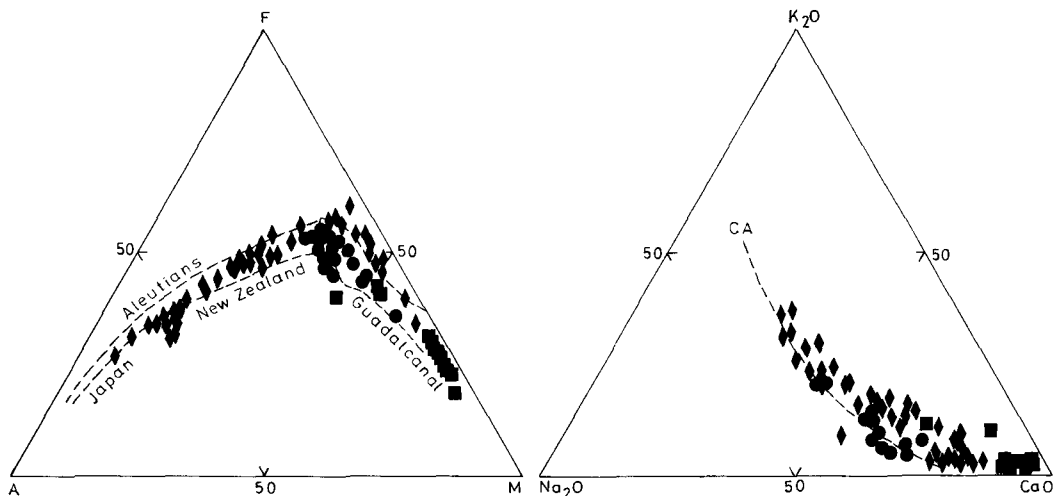


FIG. 4. AFM (A) and Na-K-Ca (B) plots for Epilchik (squares), Tigil (dots) and Machevna (rhombs) plutons from the North Kamchatka arc. Magmatic arc trends on AFM diagram (A) and average calc-alkaline trend on the Na-K-Ca diagram (B) are from Brown (1982). Plutonic rocks from the Olyutor Range plot along the typical calc-alkaline arc trends consistent with their derivation in a magmatic arc setting.

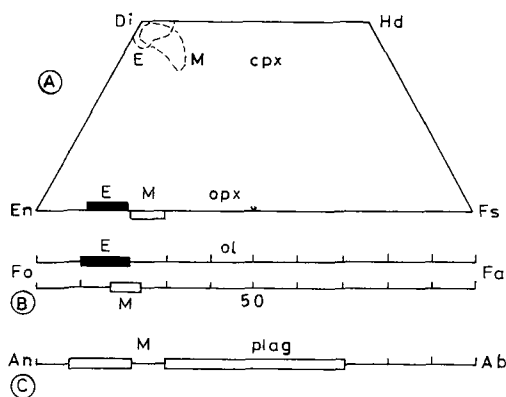


FIG. 5. Composition of pyroxenes (A), olivines (B) and plagioclase (C) in North Kamchatka arc plutons. E-E-type (ultramafic to mafic) plutons, M-M-type (mafic to intermediate) plutons.

Spinel. Microprobe analyses of the spinels are listed in Table 1. All dunite samples carry Cr-rich spinel, while both Cr-spinel and Cr-rich magnetite occur in wehrlites and pyroxenites from the transitional zone. Cr_2O_3 contents in spinels from Epilchik plutons range from 19.8 to 32.3 wt.%. A subtle difference exists between the spinels from the West and East Epilchik plutons. While West Epilchik spinels display wider variations in Cr-concentrations, East Epilchik plutons only show a relatively narrow range of Cr# [Cr/(Cr + Al) Table 1]. Spinel from wehrlites and olivine

pyroxenites have relatively low Mg# and Cr# compared with the dunite Cr-spinels.

In general, spinels from the East Epilchik pluton have lower total Fe and higher Al and Mg contents than the West Epilchik pluton oxides. Wehrlites and olivine pyroxenites from the West Epilchik pluton carry high-Cr magnetite (3.4–3.9 wt.% Cr_2O_3) which is compositionally similar to the Cr-Fe oxides reported for felsic plutons of the Olyutor Range (Kepezhinskias and Savichev, 1991).

Fig. 6 illustrates the compositional difference between spinels from individual plutons within the Olyutor Range. Spinel from the East Epilchik dunitess contain less Fe^{3+} and Ti than the other plutons and plot closer to the ophiolitic spinel field. Zoned spinels from wehrlites and pyroxenites for the same massif define a trend towards Fe-rich compositions ending in the field for oxidised, Alaskan-type spinels. The analogy is further supported by the $100\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ versus $100\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Al} + \text{Cr})$ plot (Fig. 7), where East Epilchik spinels cluster around relatively low-Fe# values in the lower portion of the Alaskan-type spinel compositions. Some spinels from the East Epilchik dunitess approach the chromite compositions from stratiform layered intrusions. The West Epilchik spinels are clearly Fe-rich, displaying significant enrichment in Fe^{3+} at high Cr_2O_3 -content (Table 1). They show a nearly continuous compositional variation, with a decrease in Cr- and Al-contents and increases in Fe^{3+} and Ti (Fig. 6). This variation of spinel

Table 1. Representative compositions of spinels in North Kamchatka plutons

	sample #		SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	TOTAL	Cr#	Mg#
dunite	E139.90	core	0.01	0.52	15.86	26.41	16.62	34.88	0.52	5.56	100.38	52.76	22.12
dunite	E139.90	rim	0.01	0.45	15.65	26.61	16.63	34.11	0.48	6.51	100.45	53.29	25.38
dunite	E139.90	core	n.d	0.65	12.38	28.89	16.90	35.19	0.48	5.77	100.26	61.02	22.61
dunite	E139.90	rim	n.d	0.57	12.49	30.21	16.13	35.33	0.27	5.13	100.13	61.86	20.57
dunite	E140.90	core	0.02	0.29	13.74	27.49	17.09	34.70	0.36	6.01	99.70	57.31	23.58
dunite	E140.90	core	n.d	0.47	12.33	26.08	18.40	35.81	0.43	5.74	99.26	58.64	22.23
dunite	E140.90	rim	0.04	0.46	12.92	25.15	18.26	35.39	0.37	5.85	98.44	56.63	22.75
dunite	E140.90	core	0.07	0.23	14.11	25.39	18.19	35.27	0.47	5.93	99.66	54.66	23.05
dunite	E140.90	rim	0.02	0.30	15.10	26.89	16.76	34.86	0.42	5.45	99.80	54.43	21.80
dunite	E144.90	core	0.01	0.74	15.22	28.00	15.46	33.90	0.35	6.06	99.74	55.24	24.16
dunite	E144.90	rim	0.02	0.75	15.59	27.84	15.56	33.92	0.41	6.22	100.31	54.50	24.63
wehrlite	E135.90	core	n.d	0.15	14.45	25.14	17.20	34.13	0.26	5.83	97.16	53.85	23.33
wehrlite	E135.90	core	0.01	0.11	14.60	22.93	18.38	34.41	0.20	6.40	97.04	51.30	24.89
wehrlite	E135.90	core	n.d	0.10	13.31	27.41	17.43	34.91	0.41	5.65	99.22	58.00	22.38
wehrlite	E135.90	rim	0.02	0.21	13.64	26.80	17.59	35.51	0.46	5.12	99.35	56.84	20.44
dunite	E108.90	core	0.01	0.43	7.83	31.29	17.63	36.60	0.47	4.10	98.36	72.83	16.63
dunite	E108.90	core	n.d	0.34	10.04	29.85	16.98	35.61	0.42	4.31	97.55	66.61	17.75
dunite	E108.90	core	0.01	0.46	7.28	33.01	16.83	36.54	0.53	3.46	98.12	75.25	14.45
wehrlite	E86.90	core	0.03	0.62	3.72	15.42	30.52	48.80	0.46	0.80	100.37	73.52	2.84
wehrlite	E86.90	core	0.10	0.69	2.21	13.68	31.43	48.80	0.61	0.75	98.27	80.59	2.66
wehrlite	E86.90	core	0.08	0.75	1.71	12.88	32.34	49.30	0.35	1.49	98.90	83.48	5.10
wehrlite	E86.90	core	0.06	0.59	3.54	14.43	30.15	47.50	0.52	1.09	97.88	73.20	3.94
wehrlite	E86.90	core	0.01	0.37	1.71	12.09	32.13	47.68	0.59	1.71	96.29	82.62	5.99
wehrlite	E86.90	rim	0.03	0.36	2.26	12.95	31.27	47.39	0.38	1.54	96.18	79.35	5.47
dunite	E19.83	core	n.d	0.42	8.17	30.86	17.88	36.95	0.42	4.05	98.75	71.69	16.36
dunite	E19.83	core	0.01	0.34	7.78	30.30	17.97	36.29	0.33	4.54	97.56	72.31	18.22
dunite	E20.83	core	n.d	0.29	8.05	31.38	17.25	36.39	0.63	3.37	97.36	72.34	14.15
dunite	E20.81	rim	0.02	0.36	8.67	31.10	17.82	37.03	0.70	3.71	99.41	70.64	15.15
dunite	E20.83	core	n.d	0.17	9.97	29.61	17.67	36.17	0.42	4.31	98.32	66.59	17.53
dunite	E20.83	rim	0.03	0.26	11.83	27.00	18.67	36.79	0.60	4.58	99.76	60.49	18.17

Fe 3+ was calculated following equation of Galan and Suarez (1989) as:

$$\text{Fe } 3+ = 2/3 (\text{Fe} - ((\text{Al} + \text{Cr})/2) - 2((\text{Ti} - ((\text{Mn} + \text{Mg})/2))))$$

Note. Cr# = 100Cr/(Cr + Al), Mg# = 100Mg/(Mg + Fe 2+).

n.d. = not detected

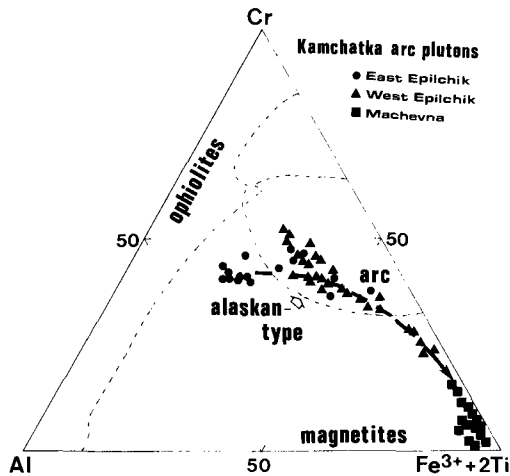


Fig. 6. Al-Cr-Fe³⁺ + Ti ternary plot for the spinels from various tectonic settings. Fields for spinels from ophiolites and Alaskan-type complexes are adapted from Jan and Windley (1990).

composition parallels the change in host rock lithology between dunites and transitional zone wehrlites and pyroxenites. Similar variations are observed in the cryptic zoning of individual oxide grains. This is demonstrated by the Mg# versus

Fe# diagram (Fig. 7) where West Epilchik dunite spinels exhibit significant zoning. Individual spinels show a significant increase in both Fe²⁺ and Fe³⁺ from core to rim, while Cr and Al contents remain relatively stable.

Spinel zoning

As noted above, spinels from both the West and East Epilchik plutons display significant compositional zoning with respect to Cr, Al, Mg and Fe concentrations. Four types of spinel zoning patterns are recognised which can be summarised as follows (normal or reverse zoning classification is based on variation of Mg# from core to rim):

Type 1: Normal zoning; from core to rim—significant increases in Cr#, Ti and Fe³⁺/R³⁺; decreases in Mg#, and Al (Fig. 8); typical of dunitic spinels of the Epilchik massifs.

Type 2: Normal zoning; from core to rim—decrease in Cr#; Mg# and Ti remain constant; rare occurrence, limited to zones impregnated by late-stage felsic melts.

Type 3: Normal zoning; from core to rim—small increase in Cr#, and a sharp increase in and higher concentrations of Ti (Fig. 8a); small decrease in Mg#; most common type of zoning.

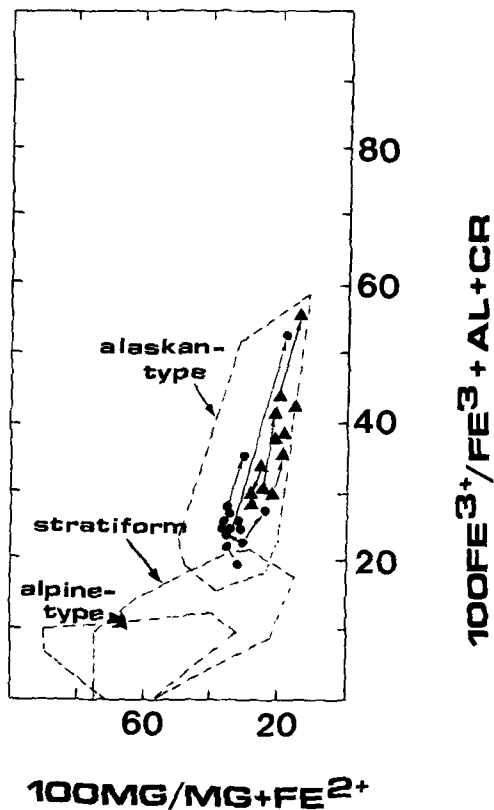


Fig. 7. $100\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ ($\text{Mg}\#$) versus $100\text{Fe}^{3+}/\text{Fe}^{3+} + \text{Al} + \text{Cr}$ ($\text{Fe}\#$) for spinels from various plutonic complexes. Fields for alpine-type, stratiform and Alaskan-type complexes are adapted from Irvine (1967). Symbols for North Kamchatka plutons are the same as in Fig. 6. Arrows refer to change in spinel chemical composition from core to rim.

Type 4: Normal or reverse zoning; from core to rim—Ti content increases, $\text{Mg}\#$ increases or shows small decrease (Fig. 8b); $\text{Cr}\#$ decreases. This pattern is typical of West Epilchik core dunites.

Significance of spinel zoning

The above data suggest that spinels from the North Kamchatka plutons show clear compositional variations between different lithologies and within individual grains. Several processes have been recognised as important factors governing these variations. Among them, pressure-temperature dependence, oxygen fugacity, bulk rock composition and sub-solidus re-equilibration with the co-existing silicates are probably the

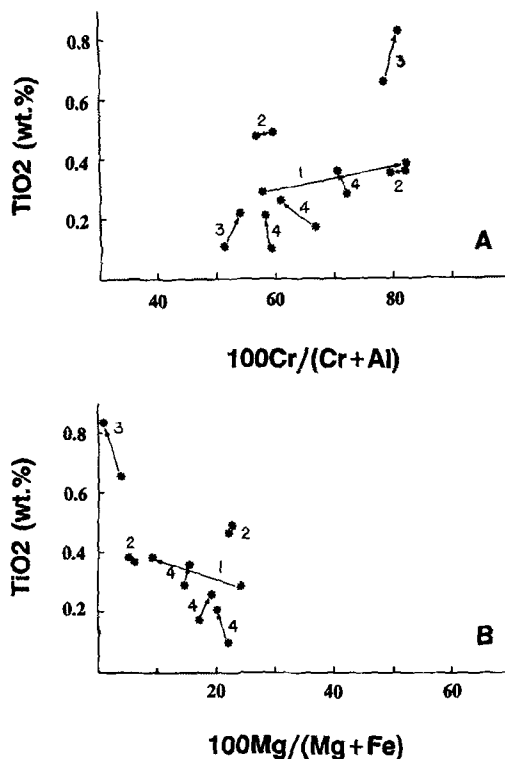


Fig. 8. $\text{Cr}\#$ (A) and $\text{Mg}\#$ (B) versus TiO_2 content for chemically zoned cumulate spinels from the Epilchik plutons. Arrows show the zoning pattern from core to rim of individual spinel crystals. Numbers refer to zoning type (see text for discussion).

most important (Irvine, 1967; Hill and Roeder, 1974; Fisk and Bence, 1980; Dick and Bullen, 1984; Roeder and Reynolds, 1991). These processes result in both normal and reverse spinel zoning patterns involving variations in Cr, Al, Fe, Mg and Ti.

Nearly the same trends can be recognised in North Kamchatka spinels on the $100\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ versus $100\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Al} + \text{Cr})$ plot (Fig. 7). Both normal (rims depleted in MgO) and reverse (rims enriched in MgO) zoning patterns appear to be representative of the Epilchik spinels suggesting variations in oxygen fugacity during crystallisation of Cr-spinels. West Epilchik spinels are markedly enriched in Fe^{3+} approaching the extreme compositions of spinels from the Alaskan-type complexes which are thought to crystallise under highly oxidized conditions in the magmatic conduit beneath the arc volcanoes (Bird and Clark, 1976). Commonly, this increase in Fe^{3+} relative to other trivalent cations is accompanied by a decrease in $\text{Mg}\#$ suggesting

general enrichment of spinel in total Fe. However, reverse trends with the Mg# slightly increasing with decreasing Fe^{3+}/R^{3+} ratio are also observed in spinels of some ultramafic cumulates from the Epilchik massifs (Fig. 7). It is possible that these reverse patterns can be explained by the sub-solidus re-equilibration of the spinel with co-existing silicate phases and will be discussed in more details in the following sections. An increase in Fe^{3+} content can be associated with increase in Mg# as observed in some spinels from the East Epilchik pluton (Fig. 7). This compositional trend correlates with oxygen fugacity variations during fractional crystallisation of the residual melt (parental for the wehrlite-olivine pyroxenite transitional zone) rather than processes of sub-solidus re-equilibration since the co-existing olivine shows progressively decreasing Fo content (Tanaka *et al.*, 1992). Pressure changes during the emplacement of the arc plutons at the shallower levels in the sub-arc crust as well as subsequent devolatilisation of the arc-related magma chambers can produce significant effects on the composition of the cumulate chromite (Roberts, 1986). The crystallisation of early Cr-rich spinel due to the reduction of Cr solubility in the parental liquid will allow a more Al-rich spinel to crystallise if the crystallisation of plagioclase is still suppressed (Roberts, 1986; Agata, 1988). This will result in enrichment of the spinel rims in Al (trends 2 and 4 in Fig. 8) as the plagioclase is not observed in the cumulate rocks of the transitional zone (Tanaka *et al.*, 1992; Kepezhinskas *et al.*, in press). However, the effect of pressure can be completely different, as suggested by experimental studies of Jaques and Green (1980) suggesting that sub-solidus Cr-spinels are significantly enriched in Cr compared to 'high-pressure' sub-liquidus spinels. This observation may apply to type 1 zoning pattern (Fig. 8) observed in some spinels from the Epilchik plutons. The increase in Cr# in these spinels is associated with their enrichment in Ti and Fe^{3+} (Fig. 8). This possibly implies that the shallow-level fractionation in the North Kamchatka arc magmatic plumbing system was coupled with significant change in oxidation conditions. Thus, it can be concluded that pressure change has a limited influence on the spinel compositions within a moderate pressure range (less than 10 kbar) or produces the reverse zoning with Cr-rich spinel rims crystallising in the shallow magmatic reservoirs (Jaques and Green, 1980; Yamamoto, 1983).

Several authors have shown that the composition of Cr-spinel is dependent on the oxygen fugacity (Hill and Roeder, 1974; Fisk and Bence,

1980). They found that with increasing oxygen fugacity Cr-spinel becomes enriched in Fe^{3+} and depleted in Mg. The Epilchik spinels define a nearly continuous trend on the Al-Cr- Fe^{3+} + 2Ti plot (Fig. 6) suggesting continuous increase of oxygen fugacity during multi-stage crystallisation of their parental magmas. This trend effectively records the change of crystallisation conditions during formation of dunite core (relatively low Fe^{3+} spinels), wehrlite-pyroxenite transitional zone (high Fe^{3+} spinels) and the gabbroic rim (Cr-rich magnetites). The other factor controlling the changes in spinel chemistry was most probably the change in bulk magma composition, from primitive Cr-rich to residual Cr-poor, accompanied by a final decrease of the total pressure during emplacement of the plutonic complex in the sub-arc crust. However, the observed complexities, in spinel zoning suggest that these primary factors were overprinted by other processes which complicated the originally more simple primary trends (Kepezhinskas and Savichev, 1991). One of the processes for changing the chemistry of spinels, is the sub-solidus re-equilibration and reaction with co-existing silicates (Roeder *et al.*, 1979; Henderson and Wood, 1981; Hatton and Von Gruenewaldt, 1985).

Effect of sub-solidus re-equilibration on spinel compositions

Sub-solidus re-equilibration of spinel with co-existing silicates (mainly olivine and orthopyroxene) can be responsible for the wide compositional variations observed in chromites from layered intrusions and ophiolite plutonic complexes. Olivine potentially has a limited influence on the Cr-Al ratio of co-existing chromite since this mineral phase contains some Cr^{3+} substituting for divalent cations in the M1 site (Schreiber and Haskin, 1976; Agata, 1988). These effects have been recognised in several layered intrusions in continental (the Bushveld complex, Hatton and Von Gruenewaldt, 1985) and island arc (Jijal complex, Jan and Windley, 1990, and Oura complex, Agata, 1988) settings.

Fine exsolution lamellae of Cr-spinel in olivine are observed in the cumulate ultramafic rocks from the Oura layered complex in Japan (Agata, 1988). The temperature estimates based on olivine-spinel thermometry fall within the range of 470–970 °C (mostly 500–800 °C). These sub-solidus temperatures also suggest significant Mg- Fe^{2+} exchange during low-temperature re-equilibration after the solidification of the ultramafic part of the Oura complex (Agata, 1988). Thus, the Mg# of the spinels can be significantly

modified during sub-solidus processes in cooling plutons and, at least partially, the low Mg# of plutonic spinels may be of non-magmatic origin. Similar Mg-Fe²⁺ sub-solidus exchange was reported from the Rhum and Bushveld layered complexes (Henderson and Wood, 1981; Hatton and Von Gruenwaldt, 1985). Consequently, the Mg/Fe²⁺ ratio can be affected by the sub-solidus chemical exchange with olivine and the lowest Mg-values observed in some North Kamchatka spinels possibly reflect subsolidus equilibration temperatures rather than the magmatic temperatures of crystallisation.

Since olivine in Epilchik dunites contains some Cr (Tanaka *et al.*, 1992; Kepezhinskias *et al.*, in press), it can potentially change the Cr/Al ratio of the co-existing spinel. However, no textural evidence for the olivine exsolution in Epilchik dunites have been observed. The spinel exhibits an euhedral or subhedral habit, and dendritic or platy spinel inclusions are not observed in the olivine. Therefore, it can be concluded that the exsolution of Cr-spinel from the olivine in the North Kamchatka plutons was negligible, and the sub-solidus re-equilibration with olivine in Epilchik dunites has not significantly affected the Cr/Al ratio of the spinels. Consequently, the observed Cr-numbers are thought to represent the original magmatic composition of cumulate spinels.

Arc spinels compared with spinels from other tectonic settings

Spinel composition is commonly used as useful tectonomagmatic indicator (Irvine, 1967; Dick and Bullen, 1984; Arai, 1992). Plutonic and volcanic complexes representing various geodynamic environments show remarkable differences in the spinel compositions. This despite the fact that sub-solidus re-equilibration with silicates and changes in oxygen fugacity during magma emplacement can affect significantly the original high-*T* composition of magmatic spinels.

The Alaskan-type plutonic complexes represent arc magma chambers (Taylor, 1967; Irvine, 1974) or arc-root complexes (DeBari and Coleman, 1989). Spinel from these complexes have significantly higher Fe³⁺ and Ti contents coupled with low-Al contents when compared to spinels from oceanic or continental rift domains. They form a distinct compositional field on the Mg# versus Fe# diagram (Fig. 7) suggesting crystallisation under high oxygen fugacity conditions (Bird and Clark, 1976). Other distinctive differences are observed in the Al-Cr-Fe³⁺ + Ti ternary plot (Fig. 6) showing practically no overlap between

the Alaskan-type complexes and MORB-type (Alpine) ophiolite spinels.

Spinel from the North Kamchatka plutons are typical of the arc environment. They have similar characteristics to spinels from the Alaskan complexes, crossing the Alaskan field on the Al-Cr-Fe³⁺ + Ti ternary plot (Fig. 6) and enclosed within the Alaskan field on the Mg#-Fe# diagram (Fig. 7). Kamchatka spinels show enrichment in total Fe, Fe³⁺ and Ti with progressive changes in rock composition from the Cr-Al spinels in dunites through the Cr-Fe-Mg spinels in wehrlites and pyroxenites towards the Cr-rich magnetites in late stage liquids (gabbros from the mafic rim).

In contrast to arc spinels, MORB spinels display a range in Cr# along with a relatively narrow range in Mg# and constant low-Ti contents (Sigurdsson and Schilling, 1976; Dick and Bullen, 1984). MORB spinels also have relatively constant ratios of Fe³⁺ to other trivalent cations (e.g. Al and Cr; see Fig. 6) suggesting a relatively low and uniform oxidation state. It is also recognised that oceanic plutonic cumulates do not contain chromites with Cr₂O₃ contents higher than 50 wt.% (Hebert, 1982). Continental stratiform complexes (e.g. Rhum, Bushveld and Skaergaard) have similar Mg#-Cr# characteristics to MORB (Fig. 7). However, these complexes tend to have slightly elevated total Fe and Fe³⁺ contents, due to higher Fe and volatile contents in the primary magmas (Campbell, 1985).

A further volcanotectonic setting which can be compared directly with the arc *sensu stricto* is the oceanic fore-arc. Recent studies of the Izu-Bonin-Mariana (IBM) arc-trench system have demonstrated that significant rift volcanism can occur between an active arc and the subduction trench (Taylor and Fujioka *et al.*, 1990; Taylor *et al.*, 1992a; Stern and Bloomer, 1992). Spinel from this environment include examples in boninites from the IBM fore-arc high, and high-Mg basaltic andesites from the associated fore-arc basin. Characteristically, fore-arc spinels have high-Cr and low-Al contents; Cr# and Mg# values being generally higher than spinels from the Kamchatka arc plutons (Fig. 9). These traits of fore-arc spinels reflect a parental magma generated from a highly refractory mantle.

Comparison between arc and ophiolitic complexes

Kamchatka data can be used as a representative suite of arc spinels which, alongside data from other environments, can help constrain the origi-

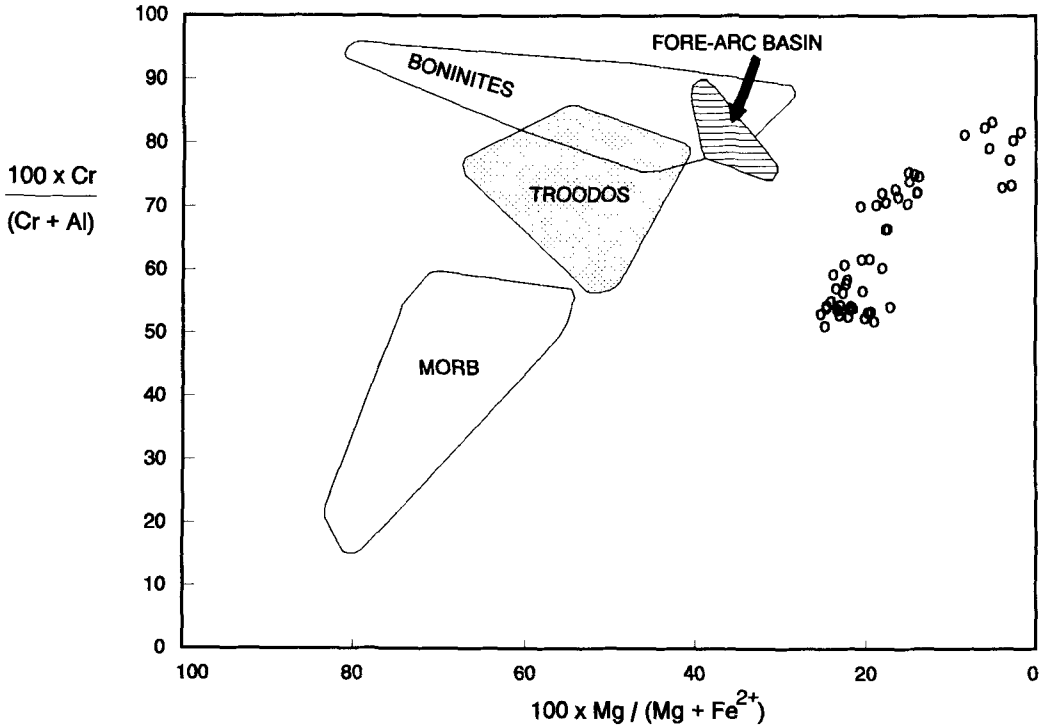


FIG. 9. $100\text{Cr}/(\text{Cr} + \text{Al})$ (Cr#) versus $100\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ (Mg#) for Kamchatka spinels (open circles) compared to spinels from boninite, fore-arc basin volcanics, low-Ti ophiolites and MORB. Data sources for MORB are the same as in Fig. 9. Other spinel data sources: boninites (Dick and Bullen, 1984; Bloomer and Hawkins, 1987); fore-arc basin (Bloomer and Hawkins, 1983); Troodos (Cameron, 1985; Thy, 1987; Thy *et al.*, 1989).

nal tectonic setting of fossil magmatic terranes such as ophiolites. While it is generally agreed that high-Ti ophiolites resemble slices of oceanic lithosphere generated in the mid-oceanic ridge or back-arc basin spreading centres, the origins of low-Ti supra-subduction zone (SSZ) ophiolites is still debatable. Possible origins for the latter include a nascent arc (Herbert and Laurent, 1990), volcanic arc (Menzies *et al.*, 1980; Phelps and Ave Lallemand, 1980; Gerlach *et al.*, 1981), rifted volcanic arc or inter-arc extensional zone (Leitch, 1984) and the fore-arc (Bloomer and Hawkins, 1983; Taylor *et al.*, 1992a).

One of the most striking differences in spinel composition between the arc plutons and low-Ti ophiolite plutonic suites is the highly oxidised nature of arc spinels. They do not plot within the typical compositional range for ophiolites on the Al-Cr-Fe³⁺ + Ti diagram (Fig. 6) suggesting that arc root complexes are typically formed at higher oxygen fugacity values than the SSZ ophiolite plutonics (Irvine, 1974). The continuous fractionation results in the formation of the late-stage Cr-rich, Ti-poor magnetites probably reflecting the general high-field strength element-depleted

nature of the arc melts (Gill, 1981). The evolved residual liquids generated by this process in arc magma chambers are saturated with the Ti-magnetite component which, under increasing oxygen fugacity, will lead to the pervasive crystallisation of the Fe-Ti oxides typical of the differentiated calc-alkaline liquids in subduction zone settings (*op. cit.*). Therefore, the evolution of the magma chambers beneath the volcanic arcs is controlled by crystal fractionation under highly oxidized conditions with the oxygen fugacity increasing while the fractionation proceeds. This implies oxidising conditions during generation and fractionation of the island arc primary magmas in sub-crustal and high-level magmatic reservoirs. This conclusion is consistent with the assumed more oxidised nature of sub-arc mantle (Ichinomegata ultramafic xenoliths, Japan) because the subduction-modified mantle above the downgoing plate undergoes a significant oxidation in addition to hydration compared to the MOR and ophiolitic mantle (Wood, 1991).

The further comparison of the different sets of the arc-related spinels on the Cr# versus Mg# diagram (Fig. 10) reveals a spectrum of compo-

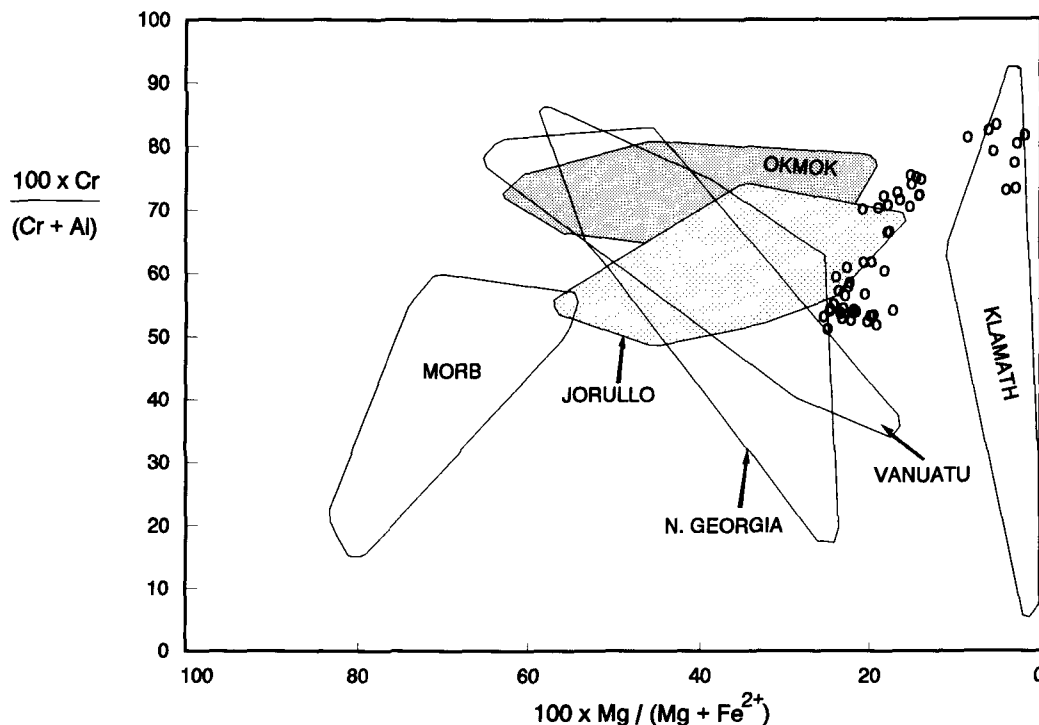


FIG. 10. $100\text{Cr}/(\text{Cr} + \text{Al})$ ($\text{Cr}\#$) versus $100\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ for Kamchatka spinels (open circles) compared to spinels from the subduction-related magmatic rocks and MORB. Data sources: MORB (Sigurdsson and Schilling, 1976; Dick and Bullen 1984); basalt from the Jorullo volcano, Mexico (Luhr and Carmichael, 1985); Mg-basalt from the Okmok volcano, Aleutian arc (Nye and Reid, 1986); Vanuatu arc anakaramite (Barsdell and Berry, 1989); North Georgia picrite, Solmon arc (Ramsay *et al.*, 1984); Klamath plutons (Snoko *et al.*, 1981; Barnes, 1983).

sitional trends from MORB-related spinels through high-Mg melts from the primitive arc settings (New Georgia, Okmok, Jorullo and Vanuatu) to the spinels from the exposed arc magmatic plumbing system such as the Klamath-type plutons. It is important to say, that, at a $\text{Cr}\#$ comparable with MORB-related spinels, the arc trend is generally parallel to the $\text{Mg}\#$ -axis showing a significant decrease (from approximately 60 to nearly 0) in the Mg content or decrease in both $\text{Cr}\#$ and $\text{Mg}\#$ (Vanuatu anakaramites and New Georgia picrites). Independently of the within-suite variations in spinel chemistry which, as it was shown earlier, could have been produced by a variety of magmatic and metasomatic processes, arc-related spinels show clear enrichments in total Fe (Fig. 10) and Fe^{3+} in particular (Fig. 6). Kamchatka arc spinels follow the Fe-enrichment trend. Other exposed arc magma chambers, for example, Klamath-type and Alaskan-type plutons' spinels commonly display decreases of $\text{Cr}\#$ during the fractionation and emplacement of the plutonic bodies (Snoko *et al.*, 1981; Bird and Clark, 1976).

Typical low-Ti ophiolites such as Troodos show distinct spinel compositional trends in cumulate plutonics on the $\text{Cr}\#$ - $\text{Mg}\#$ plot (Fig. 9). Spinel compositional fields for boninites, fore-arc basin volcanics and MORB are compared on this diagram. Boninite and fore-arc spinels are characterised by an extremely refractory nature which is consistent with their derivation through the partial melting of shallow residual mantle under high temperature and low oxygen fugacity (Van der Laan *et al.*, 1989). Since boninites and other fore-arc magmas represent the earliest stages of subduction (Crawford *et al.*, 1989; Pearce *et al.*, 1992), the oxygen conditions could possibly resemble those of MORB rather than those of the primary melts derived from the mantle modified by the subduction process (Wood, 1991). However, the boninite field spreads towards higher total Fe contents possibly reflecting initial increases of oxygen activity in the SSZ mantle. The $f\text{O}_2$ variation could possibly increase since the slab continues to descend and dehydrate. The slight shift of the fore-arc basin spinel field towards the typical arc spinels (represented by

spinel compositions from the Kamchatka arc ultramafic to mafic plutons) can possibly record the initiation of this process. It can be concluded that fore-arc magmas record the oxidation infancy in the nascent subduction zone setting while Alaskan-type (including Klamath and Kamchatka) magmas reflect the maturity of the redox conditions in the sub-arc upper mantle-lower crust system. Troodos ophiolite spinels resemble the chemistry of boninitic spinels by having Mg# greater than 40 (Fig. 9). However, relatively oxidised spinels were reported from the uppermost mafic plutonics (Herbert and Laurent, 1990). It may not be very far from reality to suggest that this part of the Troodos plutonic complex was formed under increasing oxygen fugacity conditions probably controlled by the involvement of the dehydrating slab in the ophiolite petrogenesis. The role of the hydrous fluids can be critical in this process allowing precipitation of large volumes of Cr-rich spinels with variable Mg-number (Roberts, 1986).

The presented comparison suggests that low-Ti (SSZ) ophiolite plutonic complexes show clear differences from the magmatic plumbing systems of the typical island arcs in terms of their spinel chemistry. Thus, the inter-arc rifting or magmatic arc-related setting for the formation of the low-Ti ophiolites is unlikely. Close compositional similarity with the boninite and arc tholeiite spinels suggest their formation in a similar setting, that is in the fore-arc spreading zone. This conclusion confirms the model of Bloomer and Hawkins (1983) that the low-Ti ophiolites resemble the rock assemblages, mineral and bulk rock compositions and trace element geochemistry of the fore-arc igneous complexes. Oxidation conditions in the source region of the primary magmas along with the oxygen activity in the evolving magmatic plumbing system appear to be among the major petrogenetic factors controlling the changes in the chemistry of the subduction zone magmas.

Further clarification of the differences between tholeiitic, calc-alkaline and boninite magmatic fluid compositions would provide useful information on the oxydation conditions during spinel genesis. Problems still remain in that the relative amounts of fluid introduced into the SSZ mantle wedge during the various stages of arc development are unknown.

Conclusions

1. Cumulate spinels are a common phase in arc plutonic complexes related to the evolution of the Eocene magmatic arc in northeastern Kamchatka.

2. North Kamchatka arc plutonic spinels show various types of chemical zoning involving variations in Cr, Al, Fe³⁺, Mg and Ti.

3. The various zoning patterns observed reflect the action of several processes including changing oxygen fugacity during pluton emplacement, subsolidus re-equilibration with silicates and changing melt composition during fractionation in the evolving arc plumbing systems.

4. Spinels from the Kamchatka plutons represent typical arc magmatic spinels and have distinctly higher Fe³⁺ contents along with lower Mg# compared to oceanic and fore-arc spinels. This suggests that the sub-arc magmatic plumbing systems are more oxidised than those from other tectonic settings.

5. Cumulate spinels from the low-Ti (SSZ) ophiolites are compositionally different from the arc spinels; they resemble high-Cr spinels from the fore-arc volcanics. This implies that the low-Ti ophiolites derive from a fore-arc rather than a magmatic arc setting.

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