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ORIGINAL PAPER

High-Mg# andesitic lavas of the Shisheisky Complex, Northern Kamchatka: implications for primitive calc-alkaline magmatism

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Abstract Primitive arc magmatism and mantle wedge processes are investigated through a petrologic and geochemical study of high-Mg# (Mg/Mg + Fe > 0.65) basalts, basaltic andesites and andesites from the Kurile-Kamchatka subduction system. Primitive andesitic samples are from the Shisheisky Complex, a field of Quaternary-age, monogenetic cones located in the Aleutian–Kamchatka junction, north of Shiveluch Volcano, the northernmost active composite volcano in Kamchatka. The Shisheisky lavas have Mg# of 0.66–0.73 at intermediate SiO_2 (54–58 wt%) with low CaO (<8.8%), CaO/Al_2O_3 (<0.54), and relatively high Na_2O (>3.0 wt%) and K_2O (>1.0 wt%). Olivine phenocryst core compositions of Fo90 appear to be in equilibrium with whole-rock 'melts', consistent with the sparsely phyric nature of the lavas. Compared to the Shisheisky andesites, primitive basalts from the region (Kuriles, Tolbachik, Kharchinsky) have higher CaO (>9.9 wt%) and CaO/Al_2O_3 (>0.60), and lower whole-rock Na_2O (<2.7 wt%) and K_2O (<1.1 wt%) at similar Mg# (0.66–0.70). Olivine phenocrysts in basalts have in general, higher CaO and Mn/Fe and lower Ni and Ni/Mg at Fo88 compared to the andesites. The absence of plagioclase phenocrysts from the primitive andesitic lavas contrasts the plagioclase-phyric basalts, indicating relatively high pre-eruptive water contents for the primitive andesitic magmas compared to basalts. Estimated temperature and water contents for primitive basaltic andesites and andesites are 984–1,143°C and 4–7 wt% H_2O. For primitive basalts they are 1,149–1,227°C and 2 wt% H_2O. Petrographic and mineral compositions suggest that the primitive andesitic lavas were liquids in equilibrium with mantle peridotite and were not produced by mixing between basalts and felsic crustal melts, contamination by xenocrystic olivine, or crystal fractionation of basalt. Key geochemical features of the Shisheisky primitive lavas (high Ni/MgO, Na_2O, Ni/Yb and Mg# at intermediate SiO_2) combined with the location of the volcanic field above the edge of the subducting Pacific Plate support a genetic model that involves melting of eclogite or pyroxenite at or near the surface of the subducting plate, followed by interaction of that melt with hotter peridotite in the over-lying mantle wedge. The strongly calc-alkaline igneous series at Shiveluch Volcano is interpreted to result from the emplacement and evolution of primitive andesitic magmas similar to those that are present in nearby monogenetic cones of the Shisheisky Complex.

Keywords Petrology · Kamchatka · Subduction · Andesite · Magma

Introduction

Most andesitic magmas erupted at convergent margins are relatively evolved, with Mg#'s (Mg/Mg + Fe) that are too

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low to have equilibrated with mantle peridotite. This observation has been central to the widely held view that subduction-related andesite most commonly forms from basalt by intra-crustal differentiation and magma mixing (Gill 1981; Thorpe et al. 1982; Grove and Kinzler 1986). There are, however, primitive andesitic lavas with relatively high MgO, Mg#, Ni, and Cr that could be in equilibrium with mantle peridotite. These rocks, which are commonly referred to as magnesian or high-Mg# andesites, are common in some modern arcs (Hughes and Taylor 1986; Straub et al. 2008) and are interesting because they are geochemically similar to bulk continental crust (Kelemen 1995), they often exhibit end-member geochemical characteristics among arc lavas (Yogodzinski et al. 1995; Kelemen et al. 2003a) and they may have been a more common magma type early in earth history (Shirey and Hanson 1983; Stern et al. 1989). Notable examples of high-Mg# andesites in modern arcs are found in the Cascades (Hughes and Taylor 1986; Baker et al. 1994; Grove et al. 2002), the western Aleutians (Kay 1978; Yogodzinski et al. 1994; Clynne and Borg 1997; Kelemen et al. 2003c), southwest Japan (Tatsumi and Ishizaka 1982; Tatsumi and Hanyu 2003), and in central Mexico (Luhr and Carmichael 1985; Blatter and Carmichael 1998; Straub et al. 2008). The genesis of high-Mg# andesites and their significance in the context of crust-mantle evolution are matters of active debate (e.g., Streck et al. 2007; Straub et al. 2008). It nonetheless seems clear, based on their end-member status among arc rocks worldwide (Kelemen et al. 2003a), that a thorough understanding of high-Mg# andesite is likely to provide important insights into the range of geochemical processes and physical conditions that are present in modern subduction systems.

Experimental studies have demonstrated that some high-Mg# andesites are multiply saturated in mantle olivine and pyroxene at 1.0–1.5 GPa and have water contents in excess of 3% (Tatsumi 1982; Baker et al. 1994). These and other experiments have lead to the hypothesis that high-Mg# andesitic liquids may be produced by low-pressure melting of mantle peridotite under hydrous conditions—an interpretation that is supported by peridotite melting experiments (Kushiro 1969; Hirose 1997). An alternative model for the genesis of high-Mg# andesitic melts involves the interaction of hydrous, SiO_2-rich melts derived from subducted oceanic crust and their subsequent interaction with peridotite (e.g., Kay 1978; Kelemen 1995; Yogodzinski et al. 1995; Tatsumi and Hanyu 2003). This model, which is based primarily on trace element and isotopic constraints, is consistent with experimental observations (Carroll and Wyllie 1989; Rapp et al. 1999) and with recent thermal models demonstrating that in many arc settings, the subducting plate may be hot enough to liberate not just hydrous fluids but also hydrous and siliceous magmas, produced by melting of eclogite or pyroxenite (van Keken et al. 2002; Kelemen et al. 2003b; Conder 2005).

Despite the basic differences between the two models for high-Mg# andesite genesis described earlier, both interpretations imply that high-Mg# andesites are a primary arc magma type that is generated below the crust–mantle boundary under hydrous conditions in the subduction zone environment. This conclusion has been questioned by studies which argue that high-Mg# andesites are produced within the crust by magma mixing and contamination by xenocrystic olivine (e.g. Kohn et al. 1989; Streck et al. 2007). These studies point to petrographic observations, such as reverse compositional zoning and dacitic melt inclusions in mafic phenocrysts, as evidence for a complex origin involving mixing and hybridization between basaltic melts from the mantle and felsic melts of crustal rocks. If correct, this model implies that high-Mg# andesites are not juvenile additions of andesitic crust or an important parental magma-type in subduction settings, but instead are produced by the interaction between mantle-derived basaltic melt and pre-existing crust.

In this paper, we present whole-rock and mineral composition data for a suite of primitive, high-Mg# (>0.65) basalts, basaltic andesites and andesites (SiO_2 from 47.9 to 57.6 wt%) from the Kurile-Kamchatka arc. Our objective is to determine if the high-Mg# andesitic lavas are primitive melts produced within the subduction zone, or hybrid magmas formed by differentiation of primitive basalts. Our results demonstrate that both the primitive andesitic lavas and basalts were liquids that equilibrated with mantle olivine and both therefore require a sub-crustal origin. These results indicate that the primitive andesitic lavas are an end-member magma type that formed at lower temperatures and with high pre-eruptive water contents compared to primitive basalts. Based on this, we suggest that volcanism at Shiveluch Volcano, which is located in the Aleutian-Kamchatka just south of the Shisheisky Complex, may be driven by the emplacement and evolution of primitive/parental andesitic magmas at relatively low-temperature and hydrous conditions, consistent with recent findings emphasizing the importance of magma mixing and amphibole fractionation in that strongly calc-alkaline system.

Geologic setting and sample locations

A large proportion of the historical subduction-related volcanism in Kamchatka is concentrated in the Central Kamchatka Depression (Fig. 1). At the heart of the Central Kamchatka Depression lies Kluchevskoy Volcano, the highest and most productive composite volcano in the Kurile-Kamchatka system (Melekestsev et al. 1991a).

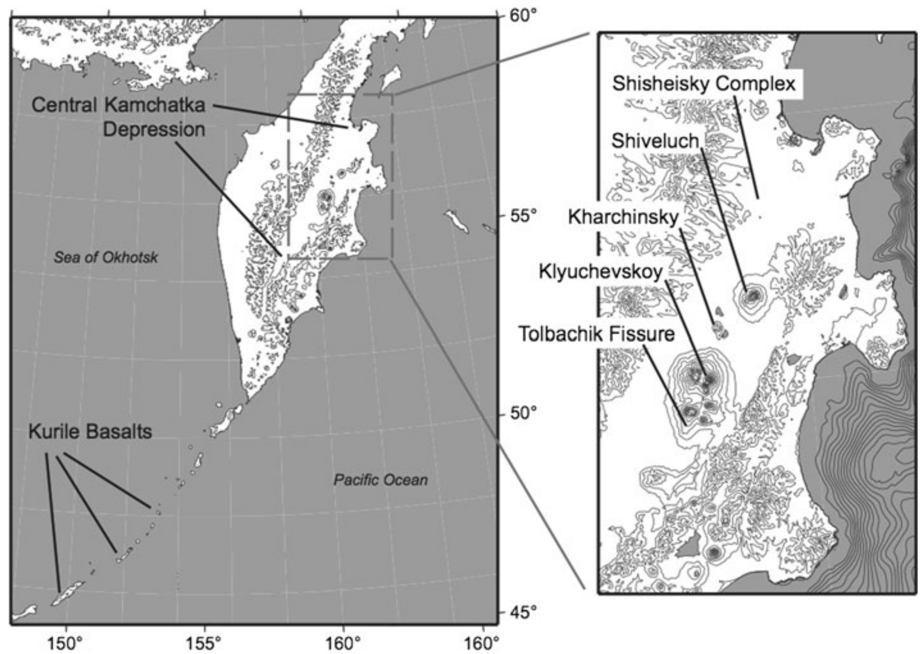

Fig. 1 Topographic and bathymetric maps of the Kurile-Kamchatka and western Aleutian subduction systems, showing sample locations and other geographic features mentioned in the text

To the south and west of Kluchevskoy, the cluster of large volcanoes sometimes referred to as the Kluchevskaya group (Melekestsev et al. 1991a) includes Ushkovsky, Bezymianny and the Tolbachik area volcanoes (Fig. 1). North of Kluchevskoy and across the Kamchatka River, Shiveluch Volcano, which is the northernmost active composite volcano in Kamchatka, lies approximately in the junction of the Aleutian and Kamchatka arcs (Fig. 1). North again from Shiveluch lies a field of Quaternary-age, monogenetic cones called the Shisheisky Complex (Portnyagin et al. 2005, 2007). The Shisheisky Complex is the source of the high-Mg# andesitic lavas that are the focus of this study (Table 1). The tectonics of the Shiveluch–Shisheisky area are interesting, because it is the place where a variety of geochemical and geophysical observations have been used to suggest that the northern edge of the subducting Pacific Plate passes westward from in front of the western-most Aleutian arc and descends into the sub-arc mantle beneath Kamchatka, thus creating a slab window beneath the Kamchatka Peninsula, north of the Aleutian–Kamchatka junction (Yogodzinski et al. 2001; Davaille and Lees 2004; Levin et al. 2005; Portnyagin et al. 2007).

This study is a petrological and geochemical comparison of high-Mg# andesitic lavas from the Shisheisky Complex with primitive basalts from five locations in the Kurile-Kamchatka system (Fig. 1; Table 1). Three of the basalt samples were dredged from submarine volcanoes in the Kurile arc (B15-88/6; B25-36/1; B25-25/3 in Table 1). The remaining primitive basalt samples are from Kharchinsky Volcano, a medium-size Quaternary-age basaltic volcano, located in the Central Kamchatka Depression between Kluchevskoy and Shiveluch (Fig. 1, see also Hochstaedter et al. 1996; Volynets et al. 1999), and from the northern vent of the 1975 Tolbachik fissure eruption (Fedotov et al. 1991). Sample locations and links to additional sample information are provided in Table 1.

Analytical methods

Rock samples were reduced with a hammer to 16–18 g of coarse, freshly broken chips, which were rinsed in distilled water and dried. These chips were crushed in a jaw crusher to less than 2–3 mm. The crushed samples were then ground to a powder in a Fritsch planetary ball mill for 30 min in an agate container. Loss on ignition was determined by heating ~4.0 grams of rock powder in quartz crucibles in a furnace for 16 h at 900°C. Preparation of glass beads for whole-rock analysis by XRF was done at the University of South Carolina following the procedures of Johnson et al. (1999). Glass beads were made from a mixture of 3.5 g of rock powder and 7 g of Li-tetraborate flux. The rock-flux mixtures were fused and quenched in graphite crucibles and molds. The fused glass beads were then re-ground in a RockLabs bench top ring mill in a tungsten-carbide container. The resultant powders were then fused and quenched in graphite for a second time. One surface of each bead was then flattened on a diamond lap. Final finishing of the flattened bead surface and analysis by XRF were done at the Washington State Geoanalytical Lab in Pullman, WA. The XRF data are reported on an anhydrous basis with major element totals recalculated to 100%

Table 1 Whole-rock major element concentrations of Shisheisky and other Kurile-Kamchatka lavas

Sample	SHISH0401	SHISH0408	SHISH0402	SHISH0405	SHISH0404	SHISH0403	SHISH0406	SHISH0409	SHISH0407	KH98-L4	B15-88/6	B25-36/1	B25-25/3	6022
Location	Shisheisky	Shisheisky	Shisheisky	Shisheisky	Shisheisky	Shisheisky	Shisheisky	Shisheisky	Shisheisky	Kharchinsk	Kurile[a]	Kurile[a]	Kurile[a]	Tolbachic
Lat ° N	57.3811	57.4434	57.3811	57.3663	57.3959	57.3751	57.3758	57.3947	57.4192	56.4391	46.758	48.200	45.883	55.6819
Long ° N	161.1795	161.2323	161.1795	161.1532	161.0434	161.2010	161.1711	161.3221	161.1137	160.8004	150.650	153.525	148.717	160.2395
Rock type	bas-and	bas-and	bas-and	bas-and	bas-and	bas-and	bas-and	and	hb-and	bas	bas	bas	bas	bas
SiO_2	53.76	54.33	54.79	54.47	54.50	54.90	53.81	57.55	62.05	50.15	49.71	50.19	49.73	51.25
TiO_2	0.71	0.66	0.64	0.63	0.72	0.99	0.81	0.73	0.53	0.89	0.84	0.72	0.96	0.95
Al_2O_3	14.95	13.79	15.79	15.70	15.05	15.73	16.83	15.85	17.67	13.97	15.91	14.80	16.45	13.81
FeO*	7.29	7.56	6.65	6.91	7.17	7.34	7.15	5.35	4.29	9.65	8.17	8.13	8.33	8.67
MnO	0.15	0.16	0.13	0.14	0.15	0.13	0.14	0.10	0.10	0.18	0.17	0.21	0.15	0.18
MgO	10.71	11.07	9.50	9.77	9.57	8.70	7.67	8.14	3.13	11.55	10.52	10.29	9.48	9.80
CaO	8.08	7.89	7.39	7.43	8.44	7.02	8.75	6.18	5.67	9.92	11.31	12.68	11.41	11.88
Na_2O	3.09	3.01	3.82	3.72	3.07	3.84	3.50	4.24	4.87	2.63	2.40	2.19	2.35	2.42
K_2O	1.06	1.36	1.14	1.10	1.15	1.16	1.13	1.66	1.50	1.03	0.82	0.64	0.95	0.84
P_205	0.21	0.18	0.15	0.13	0.19	0.21	0.21	0.20	0.19	0.21	0.16	0.13	0.19	0.21
LOI[b]	0.28	−0.09	−0.05	−0.33	0.13	0.45	0.05	−0.18	0.25	0.53	0.08	−0.22	0.67	−0.37
Mg#[c]	0.72	0.72	0.72	0.72	0.70	0.68	0.66	0.73	0.57	0.68	0.70	0.69	0.67	0.67

Whole-rock major element concentrations were determined by X-ray fluorescence spectrometry (XRF) reported here on an anhydrous basis and normalized to a total of 100%. Pre-normalization analytical totals for these samples were between 99.3 and 100.7%. Rock name abbreviations are basalt (bas), basaltic andesite (bas-and), andesite (and) and hornblende andesite (hb-and). Additional information about the XRF method can be found at http://www.sees.b wsu.edu/Geolab/note.html

[a] Additional information (in Russian) about the Kurile dredge sample locations can be found at http://www.kscnet.ru/ivs/grant/grant_06/06-3-A-08-326/index.html

[b] Loss on ignition is in weight percent. A negative loss reflects a weight gain during heating

[c] Molar Mg/Mg + Fe calculated using the total whole-rock Fe composition (FeO*)

(Table 1). Additional information on XRF procedures can be found by following the Web link listed in the notes to Table 1.

An aliquot of each agate-ground rock powder was mixed in equal proportion with a lithium tetraborate flux and prepared for trace element analysis by ICPMS (inductively coupled plasma mass spectrometry). The rock-flux mixtures were fused in graphite crucibles at 1,000°C for 30 min. The resultant glasses were powdered in a carbon-steel ring mill. Aliquots of these powders (250 mg) were dissolved in screw-cap Teflon PFA vials in a mixture of HNO_3 (2 ml), HF (6 ml) and $HClO_4$ (2 ml) at 110°C. The resulting solutions were evaporated to dryness and then re-dissolved in $HClO_4$ (2 ml) at 160°C. After the second evaporation, the samples were warmed on a hotplate and brought into a solution of H_2O (10 ml), HNO_3 (3 ml), H_2O_2 (5 drops), and HF (2 drops). Solutions were analyzed at a final dilution of 1:4800 on a model 4500 ICP-MS. All sample preparation and analytical steps for ICPMS were done at the Washington State University Geoanalytical Lab in Pullman, WA. Additional information on ICPMS procedures can be found by following the Web link listed in the notes to Table 2.

Olivine phenocryst compositions were measured on polished and carbon-coated thin sections, using the Cameca SX50 electron microprobe at the University of South Carolina. Most elements were measured with an accelerating voltage of 20 kV, a beam current of 20 nA, and count times of 30 s. Standardization was based primarily on Smithsonian microprobe standards, including the Springwater olivine (Mg), Natural Bridge diopside (Si, Ca), and the Rockport fayalite (Fe). Metals were used for standardization of Mn and Ni. Concentrations of Ni and Ca in olivine were measured with count times of 100 s. Olivine results for all elements were monitored and corrected on the basis of repeat analyses of and the San Carlos olivine standard, which are reported in Table 3.

Results

Consistent with other recent studies (Portnyagin et al. 2007), the Shisheisky lavas are predominantly magnesian basaltic andesites with 53–55% SiO_2, 7–11% MgO, 6–8% FeO*, and 7–9% CaO (Table 1). One sample is a true andesite (#0409) with somewhat higher SiO_2 (57.6%) and lower MgO (8.1%), FeO* (5.4%), and CaO (6.2%). As a group, these and other Shisheisky lavas are among the most primitive in Kamchatka with Mg#'s falling mostly in the range of 0.68–0.73, and with high Ni (121–243 ppm) and Cr (371–880 ppm), and low FeO*/MgO < 0.9 (Table 1; Fig. 2, see also Fig. 3 in Portnyagin et al. 2007). One Shisheisky sample is a glassy, hornblende-bearing andesite that is more felsic (62.0% SiO_2) and clearly more evolved than the other Shisheisky lavas, with lower MgO (3.1%), FeO* (4.3%), CaO (5.7%) and Mg# (0.57, Table 1). Compared to our collection of primitive basalts from the Kuriles and Kamchatka, the Shisheisky lavas have lower TiO_2, FeO*, CaO, and CaO/Al_2O_3, and higher SiO_2 Na_2O, Al_2O_3, and K_2O at similar whole-rock Mg# (Table 1; Fig. 2). All of the lavas considered here, including published and other data from Kluchevskoy and Shiveluch volcanoes, define medium-K igneous series (Fig. 2), typical of island arcs and transitional oceanic/continental arc settings such as Kamchatka (Gill 1981).

Petrographically, the Shisheisky lavas are fresh and sparsely phyric, with always less than 15–20% modal phenocryst and micro-phenocryst abundances, indicating that the whole-rock compositions may reasonably be interpreted to be liquids. This is clearest for the Shisheisky andesite (sample #0409), which has the highest SiO_2 content among the primitive lavas (Mg# > 0.65), as well as the highest Mg# (0.73). This sample is almost completely aphyric, containing only microphenocrysts of olivine in a groundmass of glass, olivine, plagioclase, pyroxene, and opaques. Perhaps the most distinguishing petrographic feature of the Shisheisky lavas is the absence of plagioclase phenocrysts from most samples (see also Portnyagin et al. 2007). The dominant mafic phenocryst in the basaltic andesites and andesite is olivine with clinopyroxene and orthopyroxene in lesser abundances. Olivine phenocrysts in the basaltic andesites and andesite show smooth, normal zonation, from core compositions of FO86-91 to rims of FO75-82 (Fig. 3a). The Ni concentrations are high at a given FO content compared to the basalts (Fig. 4a). Concentrations of Ni are also high relative to Mg, and Mn concentrations are low relative to Fe in olivine phenocrysts from the primitive andesites compared to the basalts. This results in a broad, inverse relationship between Ni/Mg and Mn/Fe for olivine phenocrysts for the primitive Shisheisky and Kurile-Kamchatka samples (Fig. 3b), similar to that observed in olivine phenocrysts in Si-rich Hawaiian tholeiites (Fig. 3 in Sobolev et al. 2007). Calcium abundances in olivine are generally lower than the basalts at a given FO content, with the exception of one basalt sample that has low-Ca olivine phenocrysts (Fig. 4b). Clinopyroxene phenocrysts are also Mg-rich with Mg# to 0.95 and showing normal and smooth core-to-rim compositional zonation. Compared to our Kurile-Kamchatka basalts, Shisheisky clinopyroxene phenocrysts have lower CaO and higher Na_2O and Cr_2O_3. Orthopyroxene is relatively rare and observed in only two samples. Chromium-spinel with Cr# (Cr/Cr + Al) of 0.65–0.74 and Mg# of 0.33–0.62 occur as inclusions in olivine phenocrysts in all olivine-bearing Shisheisky lavas. These compositions are similar to spinel in the high-Mg# basalts and to peridotite xenoliths

Table 2 Whole-rock trace element concentrations (ppm) of Shisheisky and other primitive Kamchatka and Kurile lavas

Sample Location Rock type	SHISH0401 Shisheisky bas-and	SHISH0402 Shisheisky bas-and	SHISH0403 Shisheisky bas-and	SHISH0404 Shisheisky bas-and	SHISH0405 Shisheisky bas-and	SHISH0406 Shisheisky bas-and	SHISH0407 Shisheisky hb-and	SHISH0408 Shisheisky bas-and	SHISH0409 Shisheisky and	B15-88/6 Kurile bas	B25-25/3 Kurile bas	B25-36/1 Kurile bas	6022 Tolbachic bas
Cr	880	530	454	719	567	371	59	818	418	531	442	395	430
Ni	243	210	242	185	233	121	21	237	234	182	165	105	107
La	8.86	7.86	10.7	9.05	7.47	9.32	12.0	7.13	10.3	8.09	9.81	6.56	9.00
Ce	19.9	17.7	23.4	20.0	16.9	20.7	25.6	15.9	22.2	18.6	22.7	14.8	21.0
Pr	2.72	2.42	3.08	2.80	2.32	2.89	3.36	2.26	2.86	2.64	3.20	2.08	2.90
Nd	12.0	10.5	13.4	12.5	10.1	12.6	13.8	10.4	12.1	12.1	14.6	9.70	12.5
Sm	3.05	2.72	3.39	3.17	2.66	3.16	3.06	2.77	2.86	3.26	3.94	2.73	3.60
Eu	0.99	0.90	1.17	1.04	0.90	1.08	0.95	0.91	0.96	1.09	1.31	0.92	1.19
Gd	3.03	2.75	3.30	3.10	2.78	3.14	2.71	2.97	2.86	3.31	3.97	2.89	3.87
Tb	0.48	0.45	0.52	0.50	0.47	0.50	0.41	0.48	0.44	0.56	0.65	0.49	0.64
Dy	2.88	2.82	3.02	3.03	2.91	3.01	2.34	3.00	2.66	3.51	4.01	3.06	3.87
Ho	0.59	0.57	0.58	0.61	0.60	0.59	0.47	0.61	0.53	0.72	0.82	0.65	0.79
Er	1.62	1.56	1.51	1.64	1.63	1.58	1.27	1.65	1.42	1.95	2.21	1.76	2.11
Tm	0.24	0.22	0.21	0.24	0.24	0.23	0.19	0.25	0.21	0.29	0.32	0.27	0.30
Yb	1.43	1.43	1.27	1.45	1.48	1.41	1.15	1.53	1.26	1.77	1.92	1.63	1.85
Lu	0.23	0.22	0.20	0.23	0.23	0.22	0.18	0.24	0.20	0.28	0.31	0.26	0.29
Ba	328	386	323	369	374	394	531	425	466	194	193	208	213
Th	1.38	1.95	1.78	1.57	1.81	1.30	2.69	1.47	2.51	1.60	1.64	1.28	0.59
Nb	3.66	2.22	6.88	2.84	2.14	4.22	2.58	2.19	5.87	2.15	2.57	1.68	1.56
Y	14.6	14.1	14.3	15.3	15.0	15.2	12.1	15.7	13.5	18.3	20.3	15.9	19.3
Hf	2.23	2.23	2.66	2.35	2.14	2.54	3.09	1.84	2.75	1.66	1.77	1.41	1.99
Ta	0.25	0.15	0.45	0.19	0.14	0.28	0.18	0.15	0.36	0.14	0.17	0.11	0.11
U	0.69	1.13	0.82	0.71	1.07	0.68	1.46	0.86	1.28	0.54	0.46	0.45	0.34
Pb	4.70	8.34	5.95	15.80	8.20	5.53	10.0	6.89	8.59	3.72	2.62	4.13	2.05
Rb	19.3	18.4	16.8	21.3	17.5	20.5	28.0	21.8	26.6	13.9	18.5	10.7	15.5
Cs	0.89	1.12	0.73	0.95	0.58	0.89	1.25	0.93	0.83	0.62	0.92	0.40	0.46
Sr	403	403	514	430	375	518	585	360	469	402	452	362	293
Sc	27.4	23.5	20.3	27.3	25.0	26.4	13.2	27.1	18.7	39.3	38.8	45.9	42.8
Zr	78.4	79.3	102.7	80.8	75.9	89.5	114.2	66.5	108.0	56.5	58.7	46.6	68.0

Whole-rock trace element data are by inductively coupled plasma mass spectrometry (ICPMS) except for Cr and Ni, which are by XRF. Additional information about the ICPMS results can be found at http://www.sees.wsu.edu/Geolab/note.html

Table 3 Olivine core compositions

Sample Rock type[a]	SHISH0401 bas-an	SHISH0402 bas-an	SHISH0403 bas-an	SHISH0404 bas-an	SHISH0405 bas-an	SHISH0408 bas-an	SHISH04 and	B15-88/6 bas	B25-25/3 bas	B25-36/1 bas	6022 bas	KH98-5 bas	SC/KA[b] Standard	% RSD[c]
SiO_2	40.63	39.66	39.95	39.90	39.60	39.68	39.58	40.37	39.62	39.81	40.15	39.75	40.53	0.5
FeO*	9.61	12.63	12.71	10.90	12.96	9.69	15.36	11.15	13.18	13.08	11.48	13.53	9.43	1.7
MnO	0.14		0.06	0.06	0.22		0.23		0.23	0.25	0.22	0.26	0.15	13.3
MgO	49.61	46.93	46.64	47.89	46.17	49.24	44.25	48.66	46.40	45.64	47.69	45.67	50.22	0.3
NiO	0.44	0.44	0.47	0.31	0.40	0.35	0.32	0.30	0.19	0.07	0.20	0.31	0.393	8.0
CaO	0.13	0.10	0.11	0.12	0.14	0.11	0.14	0.16	0.24	0.26	0.25	0.16	0.073	8.0
Total	100.58	99.76	99.94	99.17	99.49	99.08	99.88	100.63	99.86	99.10	99.98	99.67	100.80	
FO	90.2	86.9	86.7	88.7	86.4	90.1	83.7	88.6	86.2	86.1	88.1	85.8	90.5	0.2

Averages of the most forsteritic compositions from the cores of olivine phenocrysts in lavas listed in Table 1

[a] Rock type abbreviations are the same as in Table 1

[b] Average result based on repeat analysis of San Carlos olivine standard SC/KA provided by G.P. Brey, Franfurt University

[c] One-sigma relative standard deviation based on repeat analyses of SC/KA

from Shiveluch (Bryant et al. 2007) and elsewhere in Kamchatka (Arai 1994). Pargasitic hornblende with Mg# to 0.74 and Al_2O_3 to nearly 13% is seen only in the hornblende andesite sample, where it occurs as a phenocryst rimmed by fine-grained oxides (opacite). Quartz xenocrysts with clinopyroxene reaction rims have been recognized in two basaltic andesite samples. A large olivine-orthopyroxene glomerocryst in the Shisheisky andesite (#0409) is interpreted to be xenocrystic on the basis of the relatively Fe-rich olivine core composition (FO83) compared to the high whole-rock Mg# (0.73) and the Mg-rich compositions of olivine microphenocrysts in that sample.

Concentrations of the large ion lithophile elements (Cs, Rb Ba, Th, La, Ce, Pb) are at similar or somewhat higher relative abundances in the Shisheisky lavas compared to the primitive basalts (Table 1; Fig. 5). The relative concentrations of the high field strength elements (HFSE) are also generally higher in the Shisheisky lavas. The opposite trend is observed for the middle-heavy rare earth elements (REE), Y and Sc, resulting in generally more fractionated REE patterns (higher La/Yb) in the Shisheisky lavas compared to the basalts (Figs. 5, 6). It is interesting to note that among the primitive Shisheisky lavas (those with Mg# > 0.65), the most primitive sample is the andesite (Mg# $= 0.73$, Table 1), which also has the most fractionated REE pattern, with a La/Yb of 8.2 compared to an average of 6.1 in the basaltic andesites (Table 2; Figs. 5, 6). In general, whole-rock trace element diversity among all lavas is the greatest at high Mg# (>0.65). For example, Ba, Zr, Y, and Sc abundances in primitive basalts, basaltic andesites, and andesites cover nearly the entire compositional range seen in more evolved, low Mg# lavas from Shiveluch and Kluchevskoy (Fig. 7).

The primitive Kurile-Kamchatka basalts have FeO*/MgO < 1 and Mg# > 0.65 at ~ 50 wt% SiO_2 (Fig. 2). Like the primitive Shisheisky lavas, the primitive basalts have high whole-rock Ni (101–268 ppm) and Cr (395–876 ppm), and olivine phenocryst core compositions of up to FO89, slightly lower than the most Mg-rich olivine phenocryst composition seen in the primitive andesites (Figs. 2, 4; Table 3). The common phenocryst assemblage in the basalts is Mg-rich olivine and clinopyroxene and calcic plagioclase ($\sim$An90). Key geochemical and petrographic features that distinguish the basalts from the primitive Shisheisky andesite and basaltic andesites are (1) the presence of plagioclase phenocrysts, (2) higher whole-rock CaO/Al_2O_3 at similar Mg# (Fig. 7), (3) lower Ni, Ni/Mg and higher Ca and Mn/Fe in olivine phenocrysts at similar forsterite content (Figs. 4, 5), (4) lower whole-rock Ni/MgO (Fig. 8), and (5) relatively flat middle to heavy REE patterns with lower abundances of Ba, U, Th, Pb and Sr, and stronger depletions in Hf, Zr, Nb and Ta relative to La, Ce, Nd, and Sm (Figs. 5, 6).

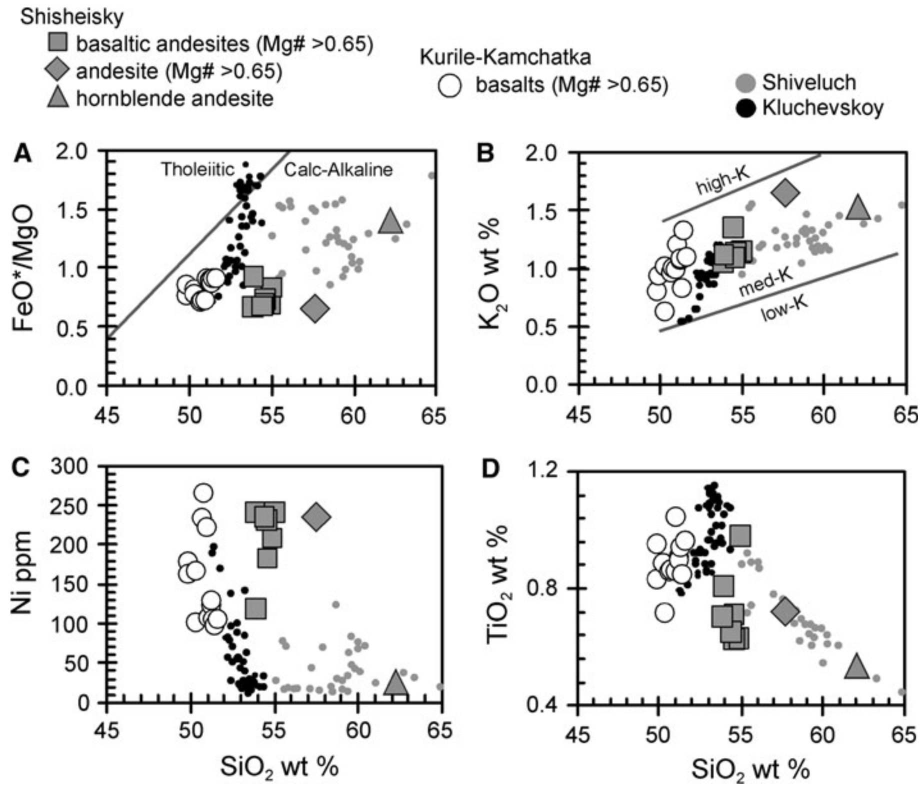

Fig. 2 Whole-rock FeO*/MgO, K_2O, Ni and TiO_2 plotted against SiO_2 for Shisheisky lavas and Kurile-Kamchatka high-Mg# basalts from Table 1. Data for Kluchevskoy are from Kersting and Arculus (1994). The calc-alkaline and tholeiitic boundary is from Miyashiro (1974)

Discussion

Olivine-melt equilibria and olivine compositions

Textural observations combined with the well-understood partitioning of Fe and Mg between olivine crystals and their enclosing melts (Roeder and Emslie 1970) provide a basis for evaluating the state of phenocryst-melt equilibria that may have been present in the primitive Shisheisky lavas and Kurile-Kamchatka basalts just prior to their eruption. Figure 9 demonstrates that, for most of our samples, the most forsteritic phenocryst core compositions are approximately in Fe–Mg exchange equilibrium with the whole-rock 'melts', assuming a equilibrium constant (Kd) of $\sim 0.30 \pm 0.03$ (Roeder and Emslie 1970). Four samples have olivine phenocryst cores that appear to be somewhat more Fe-rich than predicted by their whole-rock compositions. None of these show clear textural evidence for the presence of cumulate olivine, which if present, would shift the whole-rock compositions to the left on the graph, leaving the most forsteritic phenocryst core compositions somewhat above the equilibrium line for a Kd of 0.30 (Fig. 9). The absence of cumulate olivine is clearest for Shisheisky andesite sample #0409 (Table 1; Fig. 9). This sample, which contains ~58% SiO_2 and is the most primitive lava in our data set (Mg# of 0.73) is nearly aphyric, containing less than 15% modal abundance of olivine microphenocrysts that are rarely more than 0.30 mm in long dimension. We interpret the relatively high Fe content of the olivine microphenocrysts in this sample to reflect the late and rapid growth of those crystals just prior-to and during eruption, similar to the Fe-rich rims on the phenocrysts in other samples (Figs. 3a, 9) and in groundmass olivine. Three other samples have olivine phenocrysts cores with somewhat higher FeO than predicted by the whole-rock compositions. Again, these samples show no clear textural evidence for cumulate olivine. We therefore interpret the somewhat elevated FeO/MgO of olivine phenocryst cores in these lavas (Fig. 6) as a sampling effect, resulting from the fact that all data for each sample was collected from a single thin section. Thus, we believe that if we cut more thin sections and measure more olivines, we would eventually find core compositions with the FeO/MgO of ~0.11 as predicted by the whole-rock composition based on a Kd of 0.3 (Fig. 9).

Overall, these results indicate that, despite the occasional xenogenic crystal observed in some samples, the predominant textural features of the lavas, combined with the simple core-to-rim compositional patterns in olivine phenocrysts, and the apparent state of equilibrium between olivine cores and whole-rock 'melts' indicate that the Shisheisky andesite and basaltic andesites represent reasonable approximations of melt compositions that have experienced relatively uncomplicated crystallization and mixing histories prior to eruption. In addition, the high-Ni and low Mn/Fe seen in olivine phenocrysts of the primitive

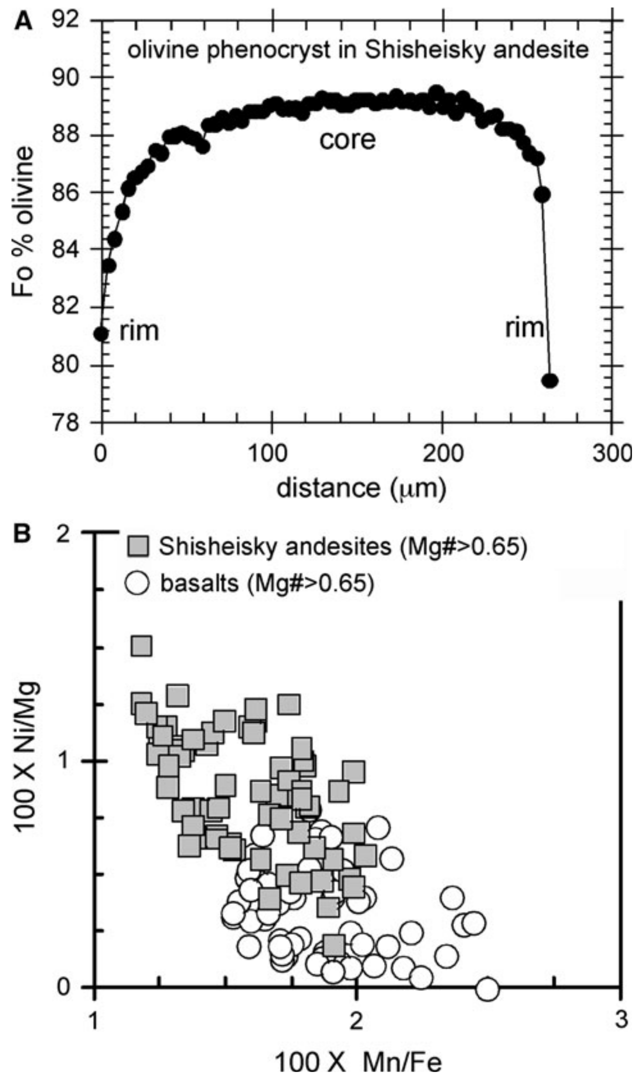

Fig. 3 Olivine phenocryst compositions in primitive Shisheisky lavas and Kurile-Kamchatka primitive basalts. **a** Shows the rim-to-rim forsterite content (Fo) of a typical olivine phenocryst in Shisheisky andesite sample #0409. **b** Illustrates the high Ni/Mg and low Mn/Fe in olivine phenocrysts from the Shisheisky andesite and basaltic andesites compared to olivine phenocrysts in the Kurile-Kamchatka basalts

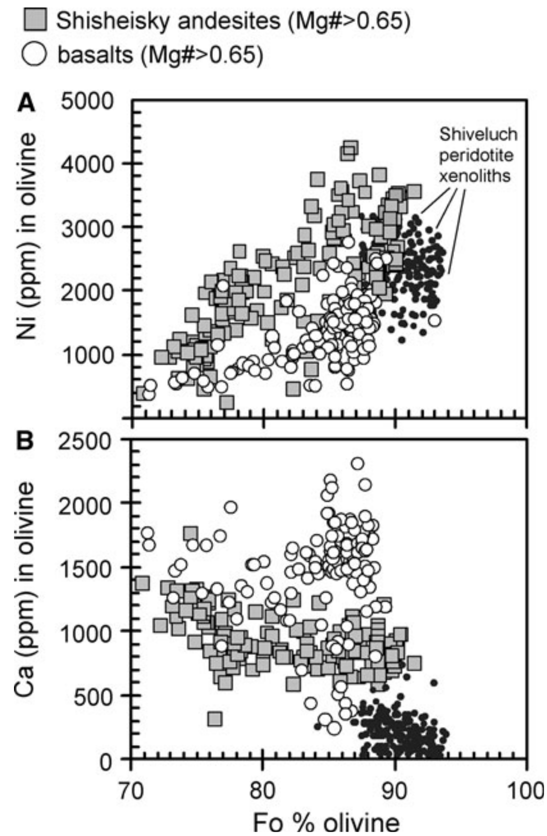

Fig. 4 Ni and Ca abundances in olivine phenocrysts plotted against olivine forsterite content (Fo) for Shisheisky andesite and basaltic andesites compared to primitive Kurile-Kamchatka basalts. Relatively high Ni content of Shisheisky olivine phenocrysts at a given Fo content compared to basalts is shown in 4A. The opposite pattern for Ca in olivine is shown in 4B. Olivine compositions in peridotite xenoliths from nearby Shiveluch Volcano (Bryant et al. 2007) are shown for comparison

Shisheisky lavas are as-expected, based on well-documented compositional controls of elemental partitioning in the olivine-melt system (Watson 1977; Hart and Davis 1978; Kinzler et al. 1990; Kohn and Schofield 1994; Wang and Gaetani 2008). Qualitatively, the Fo-rich olivine phenocrysts in the Shisheisky andesites have relatively high Ni/Mg and low Mn/Fe (Fig. 3b), consistent with the effects of olivine growth in a relatively silica-rich and therefore polymerized andesitic melt, wherein partition coefficients for most elements are shifted upward by variable amounts (Ni > Mg > Fe > Mn), resulting in olivine compositions that contain relatively high Ni/Mg and low Mn/Fe (see Fig. 7 in Wang and Gaetani 2008). Quantitatively, the level of melt polymerization can be estimated from the whole-rock major element data, based on the ratio of non-bridging oxygens to tetrahedral oxygens that they contain (NBO/T, see Mysen et al. 1982). The NBO/T values for the Shisheisky andesites fall in the range of 0.39–0.44, indicating that they are somewhat more polymerized than the Kurile-Kamchatka basalts, which have NBO/T of 0.54-0.57. Experimental results of Wang and Gaetani (2008) indicate that these differences in whole-rock melt polymerization predict values for olivine/melt distribution coefficient for Ni (D_{Ni}) in the range of 16–19 for the Shisheisky andesites and 12–13 for the basalts (Fig. 7 in Wang and Gaetani 2008). These values compare well with the observed Ni concentrations in the most Mg-rich phenocryst cores compared to the whole-rock Ni abundances, which translate into observed or apparent D_{Ni} values of 14–18 for the Shisheisky andesites and 10–15 for the basalts. This means that the Ni contents of olivine phenocrysts of the lavas, in addition to their Fe

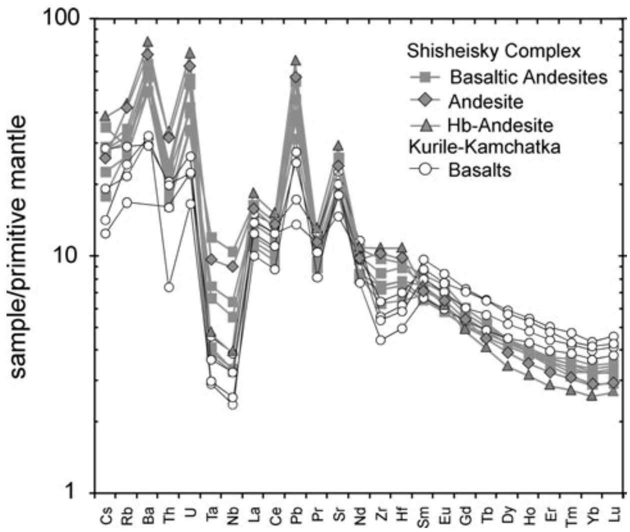

Fig. 5 Incompatible trace element concentrations normalized to primitive mantle (McDonough and Sun 1995) for Shisheisky lavas compared to primitive Kurile-Kamchatka basalts. The Shisheisky samples have generally higher abundances of large ion lithophile elements (Cs–La on this diagram) and high field strength elements (Ta, Nb, Zr, Hf), but lower middle and heavy rare earth elements (Eu–Lu) compared to the basalts. Depletions in Ta–Nb relative to La are less well expressed in the Shisheisky samples than in the Kurile-Kamchatka basalts. Depletions in Zr–Hf relative to Sm are present in the basalts but not in the Shisheisky samples. These data are from Table 2

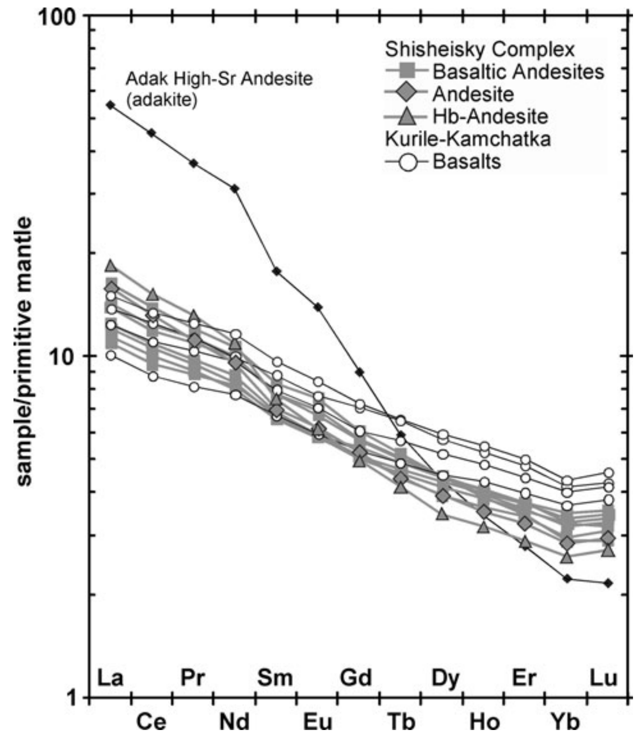

Fig. 6 Rare earth element concentrations normalized to primitive mantle (McDonough and Sun 1995) for Shisheisky lavas compared to primitive Kurile-Kamchatka basalts. The Shisheisky lavas have slightly lower abundances of middle and heavy rare earth elements and more fractionated rare earth patterns than typical primitive Kurile-Kamchatka basalts. These data are from Table 2

and Mg abundances, are approximately in equilibrium with their whole-rock melt compositions, again supporting the conclusion that the Shisheisky andesites are a primitive magma type that has chemical and physical properties unlike those of typical arc basalts, but like arc basalts, was probably also equilibrated with mantle olivine shortly prior to eruption (Portnyagin et al. 2007).

Temperatures and water contents

The absence of plagioclase phenocrysts from most of the Shisheisky samples is a common feature of primitive, high-Mg# andesitic lavas and is widely interpreted to imply that these melts existed under conditions of relatively high dissolved water contents prior to their eruption (Tatsumi and Ishizaka 1982; Luhr and Carmichael 1985; Blatter and Carmichael 1998; Carmichael 2002). The effects of melting-point depression for silicate phases, which have been widely demonstrated through experimentation on hydrous magmatic systems (Baker and Eggler 1987; Housh and Luhr 1991; Sisson and Grove 1993a), indicate that high water contents at similar to somewhat lower MgO contents should lead to significantly lower pre-eruptive melt temperatures for the Shisheisky andesites compared to the Kurile-Kamchatka basalts.

We calculated temperatures for the Shisheisky andesites and Kurile-Kamchatka basalts using the Ca-in-olivine thermometer of Köhler and Brey (1990) and the multiply saturated liquid thermometer of Sisson and Grove (1993b). The results of these calculations are presented in Fig. 10. A pressure term of 1.2 GPa was used in both calculations. The Sisson and Grove thermometer yielded temperatures of 984–1,011°C for the Shisheisky andesites and 1,182–1,218°C for the primitive basalts. The Ca-in-olivine thermometer gives similar results, with temperatures of 1,073–1,143°C for the andesitic samples and 1,149–1,227°C for the basalts. For the Sisson and Grove thermometer, we used water contents of 7 wt%, which may be too high, causing these temperatures to be slightly lower than the Ca-in-olivine temperatures. In Fig. 10, we show the consistency of our Ca-in-olivine temperature results with hydrous experimental studies on primitive andesites and with hydrous peridotite melting experiments (Tatsumi 1982; Baker et al. 1994; Hirose 1997; Gaetani and Grove 1998), indicating that these are reasonable estimates of pre-eruptive temperature for these melts.

Pre-eruptive water contents were estimated using Sisson and Grove (1993b) and the 'tholeiitic index' method of Zimmer and Plank (2006). The tholeiitic index method

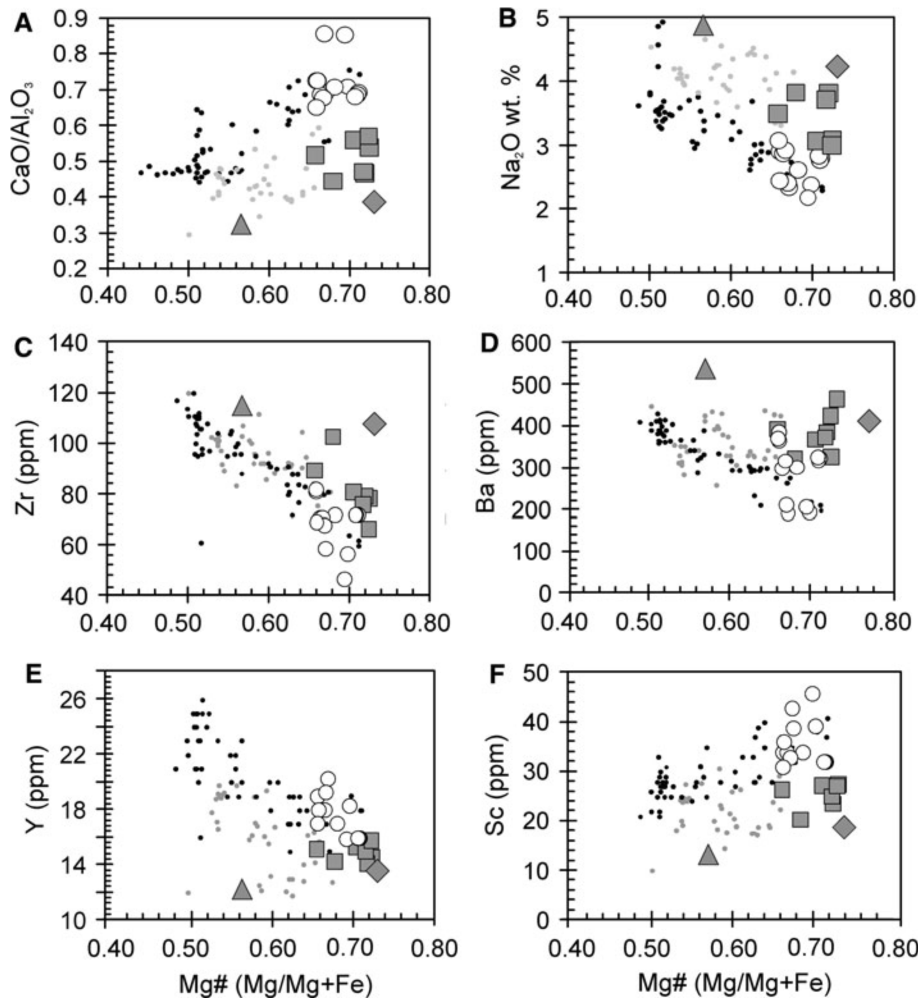

Fig. 7 Whole-rock major and trace element concentrations and ratios plotted against Mg# for primitive Kamchatka-Kurile basalts and lavas of the Shisheisky Complex compared to Kluchevskoy and Shiveluch volcanoes. Symbols here are the same as in Fig. 2. Data from Kluchevskoy Volcano are from Kersting and Arculus (1994)

predicts water contents of approximately 7 wt% for the Shisheisky andesites and 2 wt% for Kurile-Kamchatka basalts. Using temperatures calculated from Ca-in-olivine, the Sisson and Grove liquid thermometer gave water contents of approximately 4 wt% H_2O for the Shisheisky lavas and 2 wt% for the primitive basalts. Overall, these results are consistent with previous studies indicating that andesitic liquids can equilibrate with mantle peridotite only at relatively low magmatic temperatures and under hydrous conditions (e.g. Kushiro 1974; Tatsumi 1982; Hirose 1997; Grove et al. 2002; Parman and Grove 2004). These results also emphasize that the physical conditions under-which the primitive andesites formed were distinct from those which created primitive basalts in the region (see also Portnyagin et al. 2007).

Fractionation and Assimilation Processes

The existence of compositionally distinctive olivine phenocrysts in basaltic and andesitic lavas that have similar MgO contents (~7–10%) and whole-rock Mg# and Cr and Ni abundances (Fig. 2) precludes the formation of the andesites by simple crystal fractionation of the basalts. This is because the effect of olivine and pyroxene fractionation from basalt will be to lower the Mg# in the melt at constant or slowly increasing SiO_2. This process, which is common in modern subduction systems (e.g., Kay et al. 1982; Crawford et al. 1987; Draper and Johnston 1992), produces large volumes of basaltic-to-andesitic lavas that have relatively low Mg#, high Al_2O_3, and FeO*/MgO and elevated concentrations of incompatible elements. The resulting 'tholeiitic igneous series' (Miyashiro 1974), which is well illustrated by Kluchevskoy Volcano (Fig. 2), is clearly distinguished from the relatively silica-rich and low FeO*/MgO calc-alkaline igneous series, which is well illustrated by the Shisheisky high-Mg# andesites and the more evolved and more abundant andesites from Shiveluch Volcano (Fig. 2).

Effects of high water contents also fail to provide a mechanism by which the Shisheisky andesites might be linked to the Kurile-Kamchatka basalts by fractionation processes. Experimental observations indicate that high

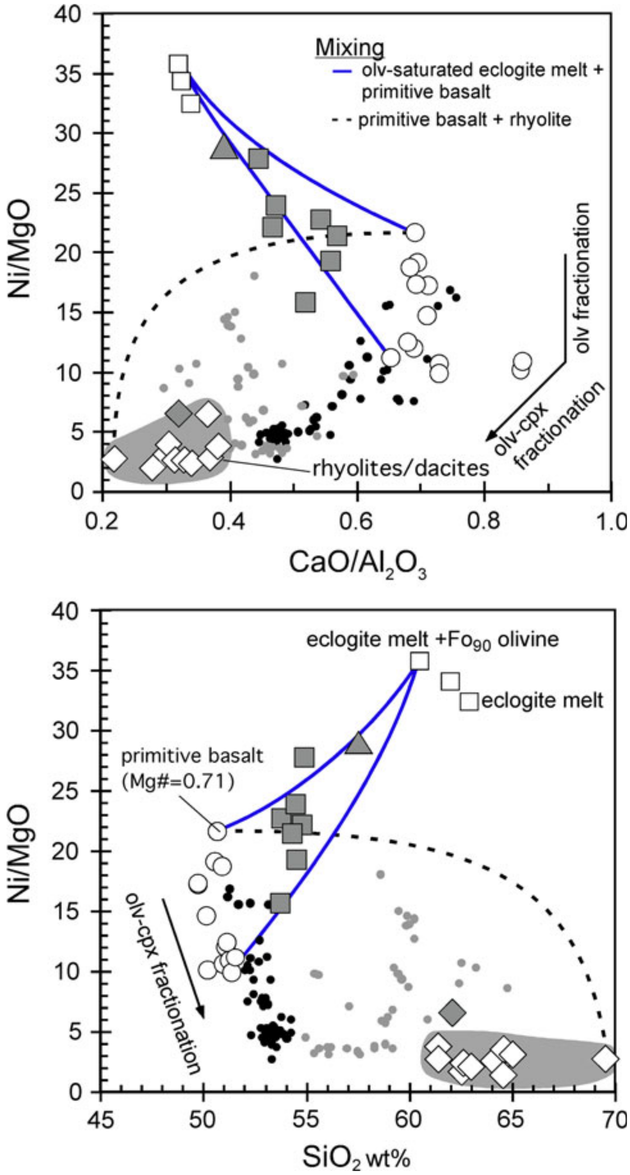

Fig. 8 Whole-rock Ni/MgO plotted against CaO/Al_2O_3 and SiO_2 for Shisheisky lavas, primitive Kurile-Kamchatka basalts and other natural and experimental melts. The correlations observed in the Shisheisky data are inconsistent with mixing between basalt and rhyolite/dacite (*dashed line*) and with crystal fractionation of olivine and clinopyroxene (*arrows*). Solid blue lines show mixtures between experimentally produced olivine-saturated eclogite melts (Wang and Gaetani 2008) and primitive basalts. Silicic mixing end-members (rhyolites/dacites) are from Izbekov (2004) and Reagan et al. (2003). Symbols here are the same as in Fig. 2

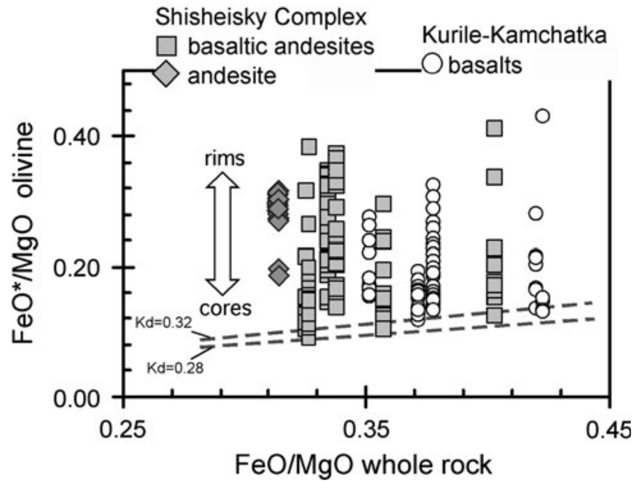

Fig. 9 Whole-rock and olivine FeO/MgO for primitive andesitic lavas of the Shisheisky Complex compared to primitive Kurile-Kamchatka basalts. *Dashed lines* are olivine and whole-rock compositions predicted to be at equilibrium based on Fe–Mg exchange coefficients (Kd's) of 0.28 and 0.32 (Kd = $[FeO^*/MgO_{olivine}]/[FeO/MgO_{melt}]$) from Roeder and Emslie (1970)

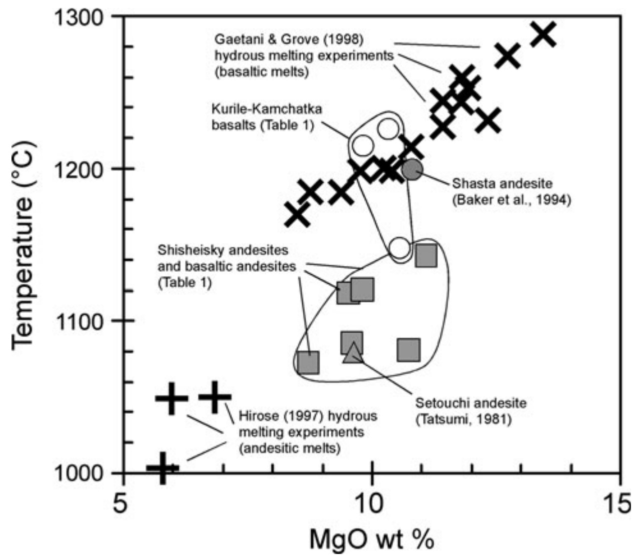

Fig. 10 Calculated temperature versus whole-rock MgO for Shisheisky Complex primitive andesitic lavas and primitive Kurile-Kamchatka basalts, based on the Ca-in-olivine thermometer of Köhler and Brey (1990). These temperature estimates are generally consistent with phase equilibrium studies on high-Mg# andesites from the southern Cascades and southwest Japan (Tatsumi 1982; Baker et al. 1994) and with hydrous peridotite melting experiments of Hirose (1997) and Gaetani and Grove (1998)

water contents in arc basalts under mid-to-lower crustal pressures result in the early onset of Fe–Ti oxide and hornblende crystallization, relative to anhydrous silicate minerals (Sisson and Grove 1993a). The effects of advanced fractionation of oxides and hornblende is to drive basaltic melts toward intermediate silica contents at approximately constant FeO*/MgO and moderate-to-high Mg#'s (Sisson and Grove 1993b). This is a well-recognized model for the genesis of some common calc-alkaline andesite assemblages (e.g., Foden 1983; Conrad and Kay 1984). The distinctive rare earth element patterns observed in some calc-alkaline andesites, especially the low Y and Yb abundances, and the concave-upward shape that is sometimes seen in the middle and heavy REE's, similar to what we observe in the Shisheisky lavas (Figs. 5, 6) are also commonly linked to crystal fractionation of hornblende in hydrous and oxidized melt systems in the middle and lower crust (Romick et al. 1992; Kay and Kay 1994; Davidson et al. 2007). The combined major and trace element characteristics of the Shisheisky andesites do not, however, support a significant role for hornblende or Fe–Ti oxide fractionation in their genesis. The important feature of the Shisheisky andesites is that they have low middle and heavy REE concentrations and slightly concave-upward REE patterns even though they lack amphibole phenocrysts and have elevated Mg#'s, consistent with an origin in equilibrium with mantle olivine (>Fo88) shortly prior to their eruption. Recognizing that effects of amphibole fractionation on the trace element patterns in calc-alkaline andesite may be present even in the absence of amphibole phenocrysts (Romick et al. 1992; Kay and Kay 1994; Davidson et al. 2007), the primitive and high MgO contents of the Shisheisky lavas and their low crystal contents strongly suggest that ratios among the REE's and other incompatible trace elements are broadly reflective of those that were derived from the source and related melting processes that preceded crystal-liquid fractionation in crustal level magma chambers. Previous studies of cumulate xenoliths from calc-alkaline systems lead us to the same conclusion. For example, the REE patterns of Mg-rich clinopyroxenes in amphibole-bearing and amphibole-free cumulate xenoliths from the Aleutians indicate that the melts that produced the amphibole-bearing xenoliths had relatively low middle and heavy REE abundances and somewhat concave-upward REE patterns prior to the onset of amphibole crystallization (cf., Yogodzinski and Kelemen 1998, 2007). Even if the fractionation of amphibole or perhaps apatite can be modeled in a way that accounts for the low abundances of middle and heavy REE's in the Shisheisky andesites, the observed differences in HFSE/REE ratios (Fig. 5), combined with the distinctive differences in minor element abundances in Fo-rich olivine phenocrysts (Figs. 3, 4), appear to decisively rule out any possible relationship between the Kurile-Kamchatka basalts and Shisheisky lavas by fractional crystallization processes (see also discussion in Portnyagin et al. 2007).

Other mechanisms that may have played a role in the genesis of the Shisheisky andesites include MASH-type processes (MASH = melting, assimilation, storage and homogenization Hildreth and Moorbath 1988) that involve the mixing of mantle-derived basalt with felsic melts produced either by extensive crystal fractionation or by melting within the crust (cf., Grove et al. 1982; Kay and Kay 1985; Annen et al. 2006). Streck et al. (2007) documented a variety of textural and mineral-compositional evidence for disequilibria in primitive andesites from Mt. Shasta, which they interpreted to be hybrid rocks, formed as dacitic crustal melts mixed with basalt and cumulate or other high-Mg# xenocrystic debris through MASH-type processes. Kohn et al. (1989) similarly concluded that some high-Mg# andesites of the Setouchi Belt in southwest Japan were derived by cumulate and mixing processes. Tatsumi et al. (2006) also present a crustal-melting and assimilation model to account for certain aspects of some primitive andesitic lavas from southwest Japan.

Textural and mineralogical features of the Shisheisky andesites and basaltic andesites, especially their low phenocryst contents and the normal core-to-rim compositional zonation observed in olivine phenocrysts (Fig. 3b), demonstrate that no significant reversals in temperature or composition were recorded during the growth of the olivine phenocrysts and microphenocrysts that are in the rocks. Our view is that these observation, combined with generally good state of olivine equilibria with the whole-rock 'melts', essentially rule out MASH-type processes like those which might be expected in crustal magma chambers. Whole-rock major element data appear to support this view. Figure 8, for example, shows that mixing between primitive basalt and dacitic-to-rhyolitic melts cannot account for the combination of high (whole-rock) Ni/MgO and low CaO/Al_2O_3 at intermediate SiO_2 observed in the Shisheisky andesites. This is primarily because the Shisheisky andesites have high Ni/MgO so their low CaO/Al_2O_3 and intermediate silica contents cannot be explained either by crystal fractionation, which would lower Ni/MgO, or by mixing between basalt and felsic crustal melts, which have low Ni/MgO and CaO/Al_2O_3 including dacites, rhyolites, granophyres, or granitic inclusions which are often cited as crustal end-members in mixing processes (Fig. 8). Other features that are difficult to explain by mixing of typical arc magma end-member compositions are the Na_2O and Al_2O_3 abundances, which are higher in the Shisheisky andesites than in typical basalt-rhyolite mixtures. Rare earth element patterns are also inconsistent with crustal-level mixing because the evolved, crustal-melt end-members in Kamchatka and similar subduction systems (e.g., Cascades, Southern Alaska) typically have relatively flat HREE patterns (normalized Dy/Yb $\sim$ 1) and prominent negative Eu anomalies (e.g., Reagan et al. 2003; Izbekov et al. 2004). Mixing between basalt and dacitic-to-rhyolitic crustal materials will therefore not produce the relatively low heavy REE abundances and smoothly curving REE patterns that lack Eu anomalies, such as those observed in the Shisheisky samples. Thus, if MASH-type process have played a significant role in the genesis of the primitive Shisheisky lavas, they can only have occurred in the uppermost mantle, involving the assimilation of orthopyroxene from harzburgite by primitive basalt, which causes the melt to evolve toward hypersthene-normative and andesitic compositions while it's high Mg# is buffered by interaction with mantle olivine (Kelemen 1990; Yogodzinski et al. 1994).

We do not of course rule out entirely the possibility that the Shisheisky lavas have mixed with or assimilated more felsic material in their ascent through the crust. The most obvious evidence of crustal assimilation in the Shisheisky andesites is the presence of quartz xenocrysts, observed in two samples, which contain phenocrysts of olivine and clinopyroxene. Several lines of evidence suggest, however, that the incorporation of these xenocrysts has not significantly affected the composition of the primitive andesites nor does it question their relevance to our understanding of mantle processes in northern Kamchatka. First, olivine and clinopyroxene phenocrysts in the Shisheisky lavas are normally zoned and have smooth core to rim transitions (Fig. 3a). This implies that olivine, which is the dominant mafic phenocryst in these rocks, has not recorded a complex evolutionary history involving mixing between mafic and felsic magmas within the crust. Second, the Fo90 olivines in the primitive andesitic lavas are in equilibrium with their whole-rock 'melts', indicating that these are mantle-derived liquids whose compositions have not been drastically altered by assimilation of felsic crust. Finally, the two samples that have quartz xenocrysts are nearly identical to those that are absent of quartz. This suggests that the Shisheisky lavas have not been significantly affected by assimilation and mixing with felsic material during their ascent through the crust. More broadly, the similarities between the Shisheisky samples and primitive andesites from other subduction systems, especially the southern Cascades and central Mexico where they are common (Luhr and Carmichael 1985; Hughes and Taylor 1986; Luhr et al. 1989; Baker et al. 1994; Borg et al. 1997; Clynne and Borg 1997; Straub et al. 2008), suggests that their intermediate silica contents and primitive (high-Mg#) and hydrous/oxidized nature are primary features related to their genesis in subduction zones, and are not produced by mixing and assimilation processes within the crust.

Melting and melt-rock reaction

Having emphasized in the previous discussion that the observed olivine-melt equilibrium, textural evidence and whole-rock geochemical features of the Shisheisky lavas are inconsistent with crystal fractionation from a basaltic parent or mixing between primitive basalts and evolved rhyolites and dacites, it should be clear that we interpret these high-Mg# andesites as liquids derived from the subarc mantle and subducting plate.

We envision two end-member processes that may lead to the formation of primitive andesites such as those from the Shisheisky Complex. One possibility is that the Shisheisky primitive andesites are low-pressure melts of mantle peridotite which was metasomatized by aqueous fluids from the subducting plate and that melted at low temperatures and pressures and under unusually hydrous/water-rich conditions. Experimental studies demonstrate that the effect of increased dissolved H_2O on the major element composition of melts in equilibrium with mantle peridotite is to increase $SiO_2/(FeO + MgO)$ in hydrous melts relative to anhydrous melts (Hirose 1997; Gaetani and Grove 1998; Falloon and Danyushevsky 2000; Grove et al. 2002; Parman and Grove 2004). The Shisheisky andesites clearly have elevated $SiO_2/FeO + MgO$ compared to normal arc basalts and could be interpreted to have formed by melting under unusually hydrous conditions (e.g., Tatsumi 1982; Luhr and Carmichael 1985; Luhr et al. 1989; Borg et al. 1997; Clynne and Borg 1997). The second possible origin for the Shisheisky primitive andesites is through a multi-step process involving the formation of a silicic melt from the subducting plate—an eclogite or pyroxenite melt—followed by the interaction of that low-Mg# melt with hot peridotite in the mantle wedge (e.g., Kay 1978; Saunders et al. 1987; Defant and Drummond 1990; Kelemen 1995; Yogodzinski et al. 1995; Stern and Killian 1996; Shimoda et al. 1998; Rapp et al. 1999; Tatsumi 2001; Grove et al. 2002; Tatsumi and Hanyu 2003).

Evaluation of whole-rock major and trace element data indicate that the Shisheisky andesites were most likely formed by a multi-step melting and melt-rock reaction process. This conclusion is guided by Fig. 11, which shows the Na_2O and TiO_2 abundances of a variety of primitive arc rocks and related experimental results, with calculations showing the expected abundances of these elements resulting from melting of normal, MORB-type mantle. Results and calculations shown in Fig. 11A indicate that the primitive Kurile-Kamchatka basalts may be produced by 8–20% melting of depleted MORB mantle, with a modest addition of Na_2O from the slab, consistent with the 'slightly non-conservative' behavior for Na as indicated by Pearce and Peate (1995) through extensive studies of trace element enrichments in island arc and back-arc lavas compared to MORB. In contrast, the displacement of the Shisheisky lavas and similar high-Mg# andesites toward high Na_2O at low TiO_2 clearly distinguishes these lavas from primitive basalts and experimentally produced peridotite melts. Based on this, we conclude that the Shisheisky andesites were produced from a depleted/low-Ti mantle that was strongly enriched in Na by addition from the subducting plate. The presence of high Na_2O (>3%) at relatively low TiO_2 (<0.75%) in several of the Shisheisky and other high-Mg# andesitic lavas is similar to that observed in Eocene-age boninites from Bonin-Mariana arc, which are interpreted to have required a strong Na-flux

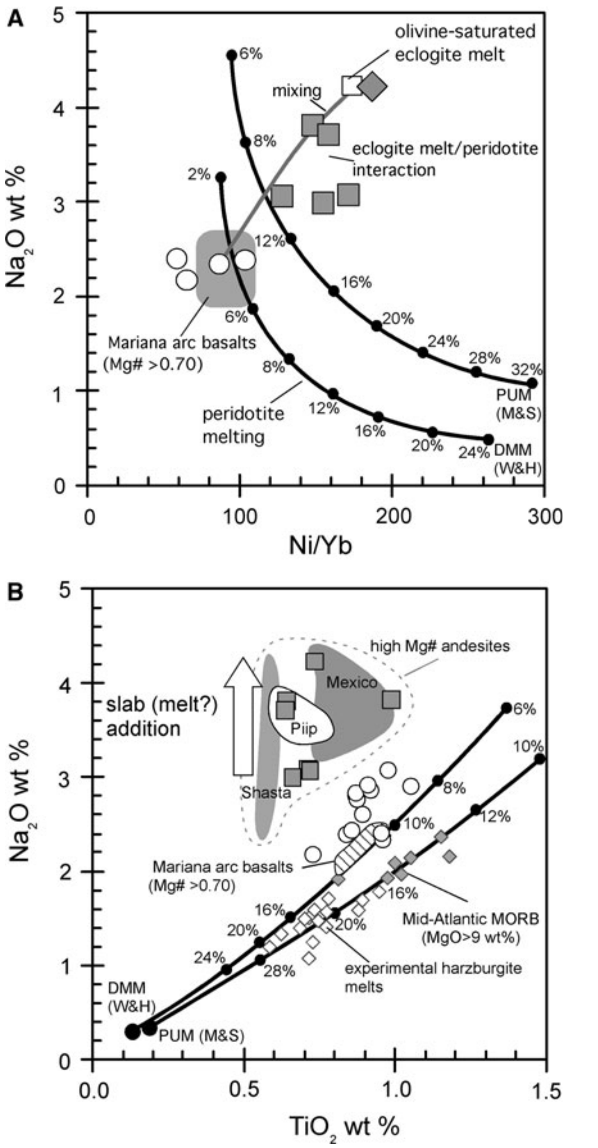

Fig. 11 Na_2O versus Ni/Yb and TiO_2 for Shisheisky Complex and Kurile-Kamchatka lavas compared to various models, natural samples and experimental compositions. Solid black lines with circles are peridotite batch melting models using the equations of Shaw (1970). Peridotite compositions are the primitive upper mantle (PUM–$Na_2O = 0.36$ wt%, $TiO_2 = 0.2$ wt%, $NiO = 0.25$ wt%, $Yb = 0.441$ ppm) from McDonough and Sun (1995) and the average depleted MORB mantle (DMM–$Na_2O = 0.28$ wt%, TiO_2 wt% $= 0.13$ wt%, $NiO = 0.24$ wt%, $Yb = 0.365$ ppm) from Workman and Hart (2005). Bulk distribution coefficients for Ti ($D_{Ti} = 0.04$) and Na ($D_{Na} = 0.02$) are from Kelley et al. (2006). Bulk distribution coefficients for Ni ($D_{Ni} = 6.7$) and Yb ($D_{Yb} = 0.115$) are from Kelemen et al. (2003c). High Na at a given Ti for high-Mg# andesites from Piip (Yogodzinski et al. 1994), Shasta (Baker et al. 1994), Mexico (Blatter and Carmichael 1998), and the Shisheisky Complex (Table 1) clearly distinguish primitive andesitic compositions from experimentally produced melts of harzburgite (Falloon and Danyushevsky 2000), primitive Mariana arc basalts (Stern et al. 1990), and Atlantic MORB (Schilling et al. 1983). The solid gray line is a mixing model between olivine-saturated eclogite melt from Wang and Gaetani (2008) and a primitive basalt from Table 1

from the subducting plate in the form of a tonalitic 'slab melt' (Pearce et al. 1992; Pearce and Peate 1995). Pearce and Peate (1995) explicitly rule out hydrous fluids as a likely metasomatic agent in the genesis of Bonin-Mariana boninites, based largely on their high Na contents. Straub et al. (2008) similarly concluded that a strong Na flux from the subducting plate in the form of a pyroxenite melt is required to explain the genesis of high-Mg# andesites and other calc-alkaline lavas in central Mexico (see additional discussion below). A broadly similar genesis for the Shisheisky lavas and primitive andesites from other locations including the Cascades (Hughes and Taylor 1986; Baker et al. 1994) and the Setouchi Belt of southwest Japan (Tatsumi 2001) seems likely (cf., Table 5 in Yogodzinski et al. 1994).

An important common denominator for all of the locations described earlier (Eocene boninites from the Mariana arc, Quaternary-age high-Mg# andesites from the Aleutian–Kamchatka junction, and modern high-Mg# andesites and related calc-alkaline lavas from central Mexico) is that they are all places where local tectonic factors are likely to have produced unusually warm subducting lithosphere, either due to it's young age (central Mexico, Straub et al. 2008) or to the details of the subducting plate geometry, involving either subduction of a plate edge (Yogodzinski et al. 2001; Portnyagin et al. 2005) or subduction initiation (Eocene Bonin-Mariana arc, Pearce et al. 1992; Pearce and Peate 1995). The tectonic setting thus leads us to conclude that the strong Na flux from the subducting plate (Na-metasomatism, Kepezhinskas et al. 1995) in all of these places is likely to have been driven by melting of the subducting plate and not simply by dehydration and hydrous fluid metasomatism (see also Kay 1978; Stern et al. 1984; Defant and Drummond 1990; Yogodzinski et al. 1995; Stern and Killian 1996; Tatsumi 2001). This implies in turn that the genesis of these primitive andesitic melts involves the interaction of Na-enriched melts of intermediate-to-silicic composition with peridotite and/or basalt in the mantle wedge. Possible effects of this interaction are illustrated in a plot of Na_2O abundance against Ni/Yb for Shisheisky and related primitive lavas (Fig. 11). Based on the relative partitioning for Ni, Na, and Yb ($D_{Ni} \gg D_{Na}$ and D_{Yb}), simple modeling demonstrates that liquids produced by variable degrees of peridotite melting will have Na_2O abundances that are inversely correlated with Ni/Yb. This is the opposite of what is observed in the Shisheisky lavas and primitive basalts (Fig. 11). Note, however, that the interaction of an eclogite-melt component (low Ni and Yb, high Na), with mantle peridotite (very high Ni, low Na), can be expected to produce a hybrid melt that has both high Ni/Yb and high Na. Experimentally produced hybrid melts formed by tonalite-olivine interaction (Wang and Gaetani 2008) have these characteristics (Fig. 11). Variable amounts of interaction between tonalitic eclogite melts and mantle peridotite, and/or mixing of the resulting hybrid melt with basalt, could then explain the positive correlation observed in Fig. 11 for the Shisheisky andesites and Kurile-Kamchatka basalts.

Straub et al. (2008) modeled the genesis of primitive andesites from central Mexico as partial melts of reaction orthopyroxenite and their interaction with mantle peridotite and basalt. In this model, reaction orthopyroxenite is formed by slab-derived hydrous and silica-rich fluids, which interacts with mantle peridotite immediately above the slab surface (Yaxley and Green 1997). Melts from the so-produced orthopyroxenite are expected to be andesitic with less than 10% MgO and 100–200 ppm Ni (Straub et al. 2008). The strong partitioning of Ni into olivine phenocrysts in these rocks results from the polymerized/intermediate silica contents and moderate MgO contents of the magmas (Watson 1977; Hart and Davis 1978; Kinzler et al. 1990; Kohn and Schofield 1994; Wang and Gaetani 2008). This model is like that of Sobolev et al. (2005), in that it proposes that olivine-bearing and high-Mg# lavas are produced by melting of an olivine-free source, but it is unlike the Sobolev model in that it does not require the existence of a high-Ni melt.

High Ni/MgO in some samples (Fig. 5) indicates that the Shisheisky basaltic andesites and andesite are unusually primitive, but it does not provide a clear basis for concluding that an unusually Ni-rich magma played a roll in their genesis. The Ni abundances in the Shisheisky lavas are mostly 200–240 ppm (Table 2). Two samples have Ni/MgO > 25 (ppm/wt%), which is significantly higher than Ni/MgO in primitive basalts selected for this study (Fig. 5). The Ni/MgO values of the most primitive Shisheisky samples are also higher than Ni/MgO in basalts throughout Kamchatka with MgO $> 8.0\%$ (Kersting and Arculus 1994; Hochstaedter et al. 1996; Portnyagin et al. 2007), but they are similar to Ni/MgO in picrites and picritic basalts from other arc locations (Nye and Reid 1986; Thirlwall et al. 1996). This confirms that the Shisheisky andesites are indeed among the most primitive arc lavas worldwide, but it also indicates that their origin does not necessarily involve a primary arc magma with a uniquely high Ni abundance.

Finally, it appears that a model involving the melting of reaction orthopyroxenite and the interaction of that silica-rich melt with mantle peridotite or basalt (Straub et al. 2008) may explain many aspects of high-Mg# andesite lavas that we have previously interpreted to result from the melting of eclogite at the surface of the subducting slab (Yogodzinski et al. 1995; Yogodzinski and Kelemen 1998; Kelemen et al. 2003c). We note, however, that textural and compositional details of certain continental and arc xenoliths (e.g., Smith and Riter 1997; Bryant et al. 2007) indicate that a reaction orthopyroxenite produced by the interaction of aqueous fluids and mantle olivine is likely to be low in Na (in addition to Ca and Al) and may therefore be an unlikely source for the Na-rich primitive andesitic melts in modern arcs. The low Na content of reaction orthopyroxenite observed in xenoliths indicates that Na is not efficiently mobilized by aqueous fluids, which again, is consistent with trace element studies of island arc and backc-arc basalts, indicating that Na is a moderately non-conservative element in subduction systems (Pearce et al. 1992; Pearce and Peate 1995). We conclude that the relatively Na-rich nature of the Shisheisky lavas indicates that the slab-derived source component that they contain was probably also Na-rich, and therefore likely to be a CPX-bearing rock, either an eclogite or pyroxenite.

Primitive calc-alkaline magmas at Shiveluch Volcano

Shiveluch Volcano, the northernmost active composite volcano in Kamchatka (Fig. 1) is the one in the Kurile-Kamchatka system most likely to have been produced by the emplacement and evolution of primitive andesitic magmas like those of the Shisheisky Complex. This is because Shiveluch rocks have higher average SiO_2 relative to FeO*/MgO than other Kamchatka volcanoes (e.g., Fig. 10b in Ponomareva et al. 2007), and in this way are similar to lavas of Piip Volcano in the western Aleutians, and Mt Shasta in the southern Cascades, where the dominant eruptive products have also been tied to primitive andesitic magmatism (Yogodzinski et al. 1994; Grove et al. 2003).

Humphreys et al. (2006, 2008) conclude that Shiveluch magmas evolve primarily by decompression-induced crystallization under volatile-saturated conditions. They also show abundant evidence for mixing by recharge from hotter and more Mg-rich magmas and by the intermittent addition of small batches of replenishing magmas that are relatively evolved (Humphreys et al. 2006, 2008). These aspects of the Shiveluch system are consistent with the evolution of primitive andesitic melts, like those of the Shisheisky Complex, which are relatively Mg-rich (Table 1), and so may be the source of xenocrystic olivine and pyroxene observed in evolved Shiveluch andesites (Humphreys et al. 2008). The Shisheisky primitive andesitic magmas also have high volatile contents and exist at low temperatures and so will quickly reach volatile-saturation as they rise into the crust and begin to decompress and degas. Compared to primitive basalts, primitive andesitic magmas are also close in temperature and viscosity to evolved Shiveluch andesites, consistent with efficient mixing following frequent, small-batch recharge events as proposed by Humphreys et al. (2006, 2008).

The relatively high abundances of MgO, Ni, Cr, and Co in Shiveluch lavas and tephra (Popolitov and Volynets 1982; Melekestsev et al. 1991b; Braitseva et al. 1997; Ponomareva et al. 2007) may also reflect a genetic link with primitive andesitic magmas. This is because if the primitive/parental magmas that feed Shiveluch are themselves andesitic, then the more evolved andesites that the volcano produces are created by lower degrees of fractional crystallization, involving a higher proportion of amphibole and oxide minerals, than would be the case if the parental magmas were basalts. This means that Shiveluch andesites will generally be more primitive (less affected by fractional crystallization, so higher in MgO, Ni and Cr) than will andesites from volcanoes where the primitive/parental magmas are basalts. Efficient mixing may also lead to greater contamination of evolved andesites by high-Mg xenocrystic olivine and pyroxene from primitive andesitic magmas than would be the case for andesites produced by higher degrees of fractionation from basalts.

Low abundances of Y and heavy REE's are also common in Shiveluch andesites (Churikova et al. 2001; Yogodzinski et al. 2001; Münker et al. 2004). We attribute these to a combination of effects, involving residual garnet in the source of the primitive/parental andesitic magmas which leaves them with slightly lower middle and heavy REE's than in basalts (Fig. 6). These characteristics of the primitive/parental magmas, combined with an enhanced roll for amphibole fractionation, consistent with the amphibole-rich phenocryst assemblage in Holocene andesites from Shiveluch, and with the existence of amphibole-rich cumulate materials in some samples (Dirksen et al. 2006; Humphreys et al. 2006), produce the low abundances of Y and heavy REE's seen in common andesites at Shiveluch.

If as we hypothesize, the Shiveluch system is driven by hydrous and low-temperature primitive andesitic magmatism, then recharge/reheating and remobilization are probably important processes that offset the pressure-quenching effects of decompression and volatile loss under H_2O-saturated conditions that would otherwise cause Shiveluch magmas to solidify into calc-alkaline plutons. Thus, the ubiquitous textural and mineral composition effects of recharge and mixing documented by Humphreys et al. (2006) are an inevitable result of the fact that such volatile-rich magmas have remained liquid long enough be erupted at the earth's surface.

Conclusions

Whole-rock and mineral compositions for high-Mg# (>0.65) lavas provide a clear basis for concluding that primitive andesitic and basaltic lavas are genetically distinct from one another. Primitive andesitic lavas from monogenetic cones of the Shisheisky complex were produced at relatively low magmatic temperatures (1,073–1,143°C) and with high pre-eruptive water contents (4–7 wt% H_2O), compared to primitive Kuriles-Kamchatka basalts, which are hotter (1,149–1,227°C) and less water-rich (2 wt% H_2O). Consistent with the local tectonic setting above the edge of the subducting Pacific lithosphere, key whole-rock geochemical parameters (high Ni/MgO, Na, La/Yb, Ni/Yb and low CaO/Al_2O_3) and mineralogical features (Ni-rich olivine phenocrysts) in the primitive Shisheisky lavas are inferred to have resulted from the interaction of silicic or intermediate composition partial melts of eclogite or pyroxenite from at or near the surface of the subducting plate, with peridotite in the overlying mantle wedge. The petrology of Holocene-age calc-alkaline andesites from Shiveluch Volcano appears to be consistent with a genesis involving the emplacement and evolution of primitive andesitic magmas similar to those observed in the Shisheisky Complex.

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