

3. Hydrated sub-arc mantle: a source for Kluchevskoy volcano/ Kamchatka

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Abstract

Oxygen isotopes ratios of olivine and clinopyroxene phenocrysts from the Kluchevskoy volcano in the Central Kamchatka Depression have been studied using CO₂- and ArF-laser techniques. Measured $\delta^{18}\text{O}$ -values range between 5.8 to 7.1 ‰ for olivine and 6.2 to 7.5 ‰ for clinopyroxene, and are significantly heavier than for minerals crystallized from typical mantle melts. Due to the relative primitive rock composition, high $\delta^{18}\text{O}$ values cannot be explained by crustal assimilation. Based on oxygen and radiogenic isotopes (Sr, Nd, Pb) the low-T altered upper oceanic crust has been identified as source of the ^{18}O -enriched oxygen. A contribution of ocean sediment is minor (<1 ‰). Significant positive correlations between $\delta^{18}\text{O}$ and some fluid-mobile trace elements (Cs, Li, Sr, Rb, Ba, Th, U, LREE) and K₂O but no correlations between $\delta^{18}\text{O}$ and fluid-mobile elements (HFSE, HREE) suggest that ^{18}O was introduced into the mantle source by a fluid phase from the altered oceanic crust. Mass balance excludes a simple fluid induced mantle melting. Instead all observations are consistent with melting a mantle wedge, which has been variably enriched in ^{18}O by slab-derived fluids. Modeling the generation of such ^{18}O -enriched mantle shows that some Ma are required for this process to occur, which requires that the mantle source of the Kluchevskoy lavas must have been part of the non-convecting wedge, which subsequently became involved in arc magmatism associated with present-day intra-arc rifting.

Introduction

There is general consensus that arc magmatism is triggered by lowering the solidus in the mantle wedge through slab-derived fluids. In some rare cases, however, melting of subducted oceanic crust may occur resulting in the magma compositions substantially different from commonly found calc-alkaline and tholeiitic arc rocks. Despite the mantle wedge is the major source of subduction zone magmatism, a significant amount of incompatible trace elements is derived from additional sources like subducted sediments or fluids from the altered oceanic crust. Plank and Langmuir (1993) could show, that normalized concentrations of special incompatible trace elements are directly correlated with sediment fluxes at arcs. Beside it radiogenic isotopes of Sr, Pb and Be were successfully used to estimate the quantity of sediment introduced in the source. More controversial is the amount of the slab fluid, introduced in the magma source. Recent calculations reach from less than 1 % (Stolper and Newman, 1994) to values up to 20 % (Ayers, 1998). The differences are mainly caused by the limited knowledge of slab fluid composition and the kind of interaction with the mantle. In this study we show the potential of oxygen isotopes as indicator for slab-derived elements in arc magmas from Kamchatka and their use to differentiate between assimilation of magmas either by young arc crust or contamination of the mantle source by sediments.

Low-temperature reactions between water and rocks at or near the earth's surface are much more effective in fractionating oxygen isotopes than magmatic processes such as melting or fractional crystallization. Therefore, oxygen isotopes are a powerful tool for tracing crustal material in basalts (Harmon and Hoefs, 1995; Kyser et al., 1982). This is based on the assumption that the oxygen isotope composition of the mantle is constant (Chazot et al., 1997; Matthey et al., 1994a; Wiechert and Hoefs, 1995) and the rocks studied represent pristine magmatic O-isotope values. It has been shown, however, that glasses and/or feldspar are very sensitive to near surface alteration causing much of the reported oxygen isotope variation in basaltic rocks. Therefore new laser ablation techniques on olivine and pyroxene are the only reliable source of information on the primary O-isotope composition of volcanic rocks and their source. The accepted range of O-isotope compositions based on these studies is 5.7 ± 0.5 ‰ SMOW (Eiler et al., 1997a; Ito et al., 1987; Matthey et al., 1994a). Eiler et al. (1997b) and Dobosi et al. (1998) showed that the range of $\delta^{18}\text{O}$ in arc volcanics is also much less than previously accepted.

A range of conventionally determined whole rock $\delta^{18}\text{O}$ values from -2.0 to 8.5 ‰ for the Kamchatka arc has been reported earlier by Ivanov and Ustinov (1988); Kersting (1991) and Pineau et al. (1999). In this study we present oxygen isotope data for olivine and clinopyroxene phenocrysts from a suite of 16 basalts and basaltic andesites

from the Holocene Kluchevskoy volcano in the Central Kamchatka Depression using the new ArF- and CO₂-laser methods. Our results prove that the variations observed are not caused by alteration and are closely correlated with some major and trace elements and Sr and Pb isotopes. From these correlations we show that the source of the ¹⁸O-enriched oxygen is hydrothermally altered oceanic crust introduced by source contamination rather than assimilation of arc crust to the mantle wedge. Furthermore, these correlations allow to identify fluid-mobile elements derived from the slab and to study chromatographic effects within the mantle wedge. The involvement of ¹⁸O-enriched hydrated mantle material in arc magmatism may be caused by the special plate tectonic and subduction setting of the Kamchatka arc, i.e. the prominent role of subduction of the Hawaii-Emperor-Chain.

Geological setting and sampling

Quaternary volcanism on the Kamchatka Peninsula in Far Eastern Russia is related to the fast subduction (9cm a⁻¹) of the Pacific below the Eurasian plate. Volcanic centers concentrate in three major zones parallel to the trench (Fig. 3-1A): (1) the Eastern Volcanic Front (EVF), (2) the Central Kamchatka Depression (CKD) and (3) the western volcanic chain of the Sredinny range (SR). The EVF consists of about 20 presently active and many more Holocene and Pleistocene volcanoes and represents the “normal” island arc volcanic chain. The SR represents the back arc and is built on a Cretaceous collision melange and Tertiary volcanics. Quaternary volcanism in the SR today concentrates on the Ichinsky volcano. SR and EVF are separated by the CKD, a 200 km wide graben structure, which includes the Kluchevskaya Group of volcanoes. This group is comprised of 12 volcanoes, all less than 50.000 years old. The largest and highest of them, the Kluchevskoy volcano (4750 m), is known as the most active arc volcano of the world with an average of 63*10⁶ t of magma outflow per year. Tephrochronology gives a maximum age of only about 7000 years (Melekestsev et al., 1989). First mention of an eruption in 1697 is found in (Krascheninnikow, 1755), historic eruptions comprise 12 flank- and over 40 summit-eruptions (summary in Khrenov et al. (1991). The last phase of eruptions started in September 1994.

Eruption products are high-Mg basalts and basaltic andesites (HMB) and high-Al basaltic andesites (HAB). This suite is explained by polybaric fractionation under hydrous conditions starting at 19 kbar and 1350°C with olivine, clinopyroxene and spinell (Ariskin et al., 1995). High water contents of ~2 % H₂O in the magma (Sobolev and Chaussidon, 1996)) cause a suppression of plagioclase crystallization resulting in a strong Al₂O₃-enrichment.

Geophysical studies (Balesta, 1991; Piip and Yefimova, 1993) document the deep structure of the Kluchevskoy basement: Cenozoic volcanic and volcanoclastic deposits extend to 8 km depth. Greenschist to amphibolite facies rocks of Mesozoic (?) age extend to the crust-mantle boundary at 30 km. A funnel-like zone of magma ascent exists at a depth of 20-50 km, which appears to connect all active volcanoes of the Kluchevskaya group with a melting region in the mantle wedge. A shallow magma chamber in the upper crust, which has been proposed for the nearby Bezymianny volcano (Utnasin et al., 1976), was not detected below Kluchevskoy volcano. The top of the Benioff zone below Kluchevskoy is at a depth of 160 km (Fedotov et al., 1985; Gorbatov, 1997).

Samples studied here were taken during field campaigns in 1996 and 1998 from all historic and several other Holocene lava flows and cinder cones on the NE and N base of the Kluchevskoy (Fig. 3-1B, Tab. 1). The historic samples enclose high-Mg basaltic andesites (HMB) from the eruptions of 1932 and 1938 and high-Al basaltic andesites (HAB) from the eruptions of 1951, 1953 and 1956. The remaining samples, exclusively HMB's, were derived from undated cinder cones or lava-flows, exposed at river profiles. Great care was taken to avoid any trace of alteration. Sample sizes were large enough (1 to >10 kg) to allow for mineral separation of olivine and pyroxene phenocrysts.

Analytical procedures

Major and some trace elements (Ba, Co, Cr, Ga, Sc, Sr, Ni, V, Zn, Zr) were measured on glass fusion discs by standard XRF analysis. The relative 2σ -error for major elements is lower than 1 % (except FeO and Na₂O with 2 %), for trace elements lower than 5 % until the limit of 20-30 ppm. Trace elements with lower abundances were determined by ICPMS. The 2σ -error of this method is estimated to be lower than 20 % for Nb and Ta, lower than 10 % for Be, Cs, Cu, Hf, Li, Y, Pb, Rb, Tl, Th and U and around 5 % for the REE. The water content was determined by Karl-Fischer-titration (2σ around 10 %).

Oxygen isotope ratios of separated grains of olivine were measured at the Geophysical Laboratory, Carnegie Institution of Washington using a Synrad Series 48 CO₂-laser. The technique is essentially the same as described in Sharp (1990). However, in contrast to Sharp (1990), oxygen is not converted to CO₂ after reaction of samples with BrF₅, but is frozen on a molecular sieve. The isotopic composition of oxygen is determined on masses 32, 33, and 34 using a Finnigan MAT-252 mass spectrometer. The oxygen standard gas has been calibrated to the SMOW scale using NBS-28 ($\delta^{18}\text{O}=9.6\text{‰}$). Analyses of NBS-28 were performed by rapid heating with a defocused

laser beam similar to that described in Spicuzza et al. (1998), in order to avoid grain size effects (Fouillac and Girard, 1996). Daily variations have been corrected by an in-house olivine standard ($\delta^{18}\text{O}=5.2\text{‰}$). The external error of this method is estimated to be better than $\pm 0.2\text{‰}$ based on five analyses of NBS-28 ($9.57 \pm 0.18\text{‰}$, 2σ), a mean of $5.85 \pm 0.06\text{‰}$ for two analyses of UWG-2, a garnet standard used at the University of Wisconsin, and an average reproducibility better than $\pm 0.2\text{‰}$ for multiple runs of olivine samples. Oxygen isotope analyses of Ca-rich pyroxene are imprecise using the CO_2 -laser technique at the Geophysical Laboratory, therefore, single pyroxene grains were measured using the ultra-violet (UV) ArF-laser in Göttingen. The technical details of the UV-laser technique for oxygen isotope analysis are described in Wiechert and Hoefs (1995). Using the UV-laser the analytical reproducibility for Ca-rich pyroxene is less than that for olivine. This may be due to the incomplete removal of glass and feldspar from the surface of pyroxene grains rather than heterogeneity of the pyroxenes. Pyroxene data have been corrected using the same olivine standard as described above, ensuring accurate and comparable calibration to the SMOW scale. The isotope ratios of Sr and Nd on the corresponding whole rocks were measured at a Finnigan MAT 262 RPQ II plus in Göttingen. The Sr and Nd isotope ratios were corrected for mass fractionation to $^{86}\text{Sr}/^{88}\text{Sr}=0.1194$ and $^{144}\text{Nd}/^{146}\text{Nd}=0.7219$ and referenced to NBS987 (0.710245) and LaJolla (0.511847). Measured values of these standards over the period of the study were 0.710262 ± 24 and 0.511847 ± 20 . Lead isotopes were corrected to NBS981 (Todt et al., 1984). 13 measurements of this standard gave a mean of $^{206}\text{Pb}/^{204}\text{Pb}=16.90 \pm 0.01$, $^{206}\text{Pb}/^{204}\text{Pb}=15.44 \pm 0.02$ and $^{206}\text{Pb}/^{204}\text{Pb}=37.53 \pm 0.05$. Blanks for Sr, Nd and Pb are $<1\text{ng}$, $<0.03\text{ng}$ and $<0.5\text{ng}$, respectively, and have no influence on the results. From continuous measurement of standards and repeated measurements of samples, total errors (2σ) less than 0.004 % for Sr and Nd, and less than 0.1 % for Pb isotopes were determined.

Analytical Results

Major and trace elements

Our samples represent high-Mg basalts and basaltic andesites (HMB) and high-Al basaltic andesites (HAB) with a restricted range of SiO_2 from 52-54 wt% but MgO from 4.6 to 11.7 wt% (Fig. 3-2, Tab. 1). The distinction between HMB and HAB follows Crawford et al. (1987).

The trace element distribution is typical for Quaternary volcanics of Kamchatka (Churikova et al., 2000) and for island arcs in general, i.e. with a relative depletion in HFSE and enrichment in LILE (Tab. 2, Fig. 3-3). The N-MORB normalized Nb_N/Yb_N ratios range from 0.8 to 1.0 and argue for a mantle source almost similarly to that of the N-MORB. The low HREE concentrations can be explained by relatively high melting degrees (~20%). Sr isotope ratios of Kluchevskoy volcano range from 0.70351 to 0.70366 and although rather primitive for an arc environment, they are slightly enriched compared to other Quaternary lavas from Kamchatka (Tab. 3, Fig. 3-4). HAB are more enriched in Sr isotopes compared to HMB. Pb and Nd isotopic ratios are MORB-like and quite uniform for all analyzed rocks (Fig. 3-4).

Major and trace element trends can be explained by olivine and clinopyroxene (1:2 mass ratio) fractionation from a parental magma, similar in composition to sample KLU-16 (Fig. 3-2). Compared to HMB's, the HAB's form a tight group in major and trace element compositions, probably because of the limited sample number and eruptions from the same magma batch close in time (1951, 1953 and 1966). Combining our data with the published data (Ariskin et al., 1995; Kersting and Arculus, 1994; Khubunaya et al., 1994) the HAB's show same scatter in major elements, LILE, K_2O/Na_2O , Ba/Zr, La/Yb. This scatter in and the weak correlation between LILE and HFSE do not allow for a single parental magma. Different melting degrees of a similar source can explain variable LILE concentrations but have only limited influence on the element ratios. Therefore we have to assume that other processes than crystallization are required to explain the major and trace element and isotopic data.

Oxygen isotopes

Oxygen isotope ratios of single olivines from different rocks vary from 5.8 ‰ to 7.1 ‰ (Tab. 3-3). Replicate samples are reproducible to within 0.1 ‰, with one exception. Results for pyroxene give a range from 5.7 to 7.7 ‰. In samples where $\delta^{18}O$ of olivine and clinopyroxene have both been determined, pyroxene is on average 0.4 ‰ heavier. Similar results are known from mantle peridotites (Chazot et al., 1997; Matthey et al., 1994b) and consistent with cpx-ol-fractionation (Chiba et al., 1989; Zheng, 1993a). Whole rock values are calculated from the mean $\delta^{18}O$ of olivine, using olivine-melt fractionation of -0.4 ‰ at 1100-1200°C (Chiba et al., 1989; Zheng, 1993a). The resulting range of 6.2 to 7.5 ‰ is clearly larger and values are distinctly higher than for typical mantle derived melts (e.g. Harmon and Hoefs (1995)).

Having established this unusual range in O-isotope composition, we will now explore correlations between $\delta^{18}\text{O}$ and other geochemical and isotopic parameters (Figs. 3-4 to 3-7; open symbols) in order to understand the origin of these variations. A steep trend is observed between O isotopes from 6.2 to 7.5 ‰ and $^{87}\text{Sr}/^{86}\text{Sr}$ from 0.70351 to 0.70366, where historic rocks tend to have higher $\delta^{18}\text{O}$ and Sr isotopic ratios compared to older Holocene samples. There are significant positive correlations between $\delta^{18}\text{O}$ and some trace elements (Cs, Li, Sr, Ba, Rb, Th, U, LREE) and K_2O , i.e. elements which are enriched in slab-derived fluids (named “fluid-mobile” elements hereafter). Strong positive correlations are also observed between the O-isotopic and elemental ratios such as $\text{K}_2\text{O}/\text{Na}_2\text{O}$, Ba/Zr , and La/Yb . A negative correlation of $\delta^{18}\text{O}$ was found with U/Th . O-isotopes also correlate negatively with compatible elements like FeO , CaO , MgO , Zn , Sc , Cr and Ni .

Some of the elemental variability is certainly due to fractionation of mafic minerals. To correct for this effect, all concentrations were recalculated to an $\text{Mg}\#70$ by addition of olivine and clinopyroxene in the mass ratio of 1:2 (Tabs. 3-1, 3-2; Figs. 3-2, 3-5, 3-6; filled symbols). Mineral major element compositions were derived from microprobe data of Kersting and Arculus (1994); trace elements were calculated using melt/liquid distribution coefficients of Dostal et al. (1983), Dunn and Sen (1994), Hart and Dunn (1993), Kennedy et al. (1993), Klöck and Palme (1988) and Villemant et al. (1981). This approach provides a crude but effective fractionation correction for all incompatible trace elements and some major elements (K, Ti, P and Al). A maximum of 30 % mineral fractionation is recalculated for most evolved HAB studied. After these calculations, fluid-mobile elements still strongly correlate with $\delta^{18}\text{O}$. Interestingly, weak correlations between those elements, which are immobile in fluids but can be transported in melts like Na, Al and HFSE (named “melt-mobile” elements hereafter) disappear after the fractionation correction. Also, the weak positive correlations between $\delta^{18}\text{O}$ and in olivine or clinopyroxene compatible elements like FeO , CaO , MgO , Cr , Co , Ni , Sc , V and Zn disappear.

Discussion

Small variations of oxygen isotope ratios without a corresponding change in radiogenic isotopes could result from crystal fractionation. Fractionation of olivine will increase the $\delta^{18}\text{O}$ of the melt by less than 0.1 ‰, which is insufficient to explain the observed oxygen isotope range (Zheng, 1993a). Crystallization of pyroxenes does not have a detectable effect on the isotopic composition. Fractionation of magnetite must be negligible because no significant depletion in FeO or TiO_2 is observed. Separation of other minerals such as plagioclase or quartz would even lower the

oxygen isotope ratio of the magma and need not to be considered. It is obvious that separation of mafic minerals is not responsible for increased oxygen isotope ratios of the Kluchevskoy lavas.

The remaining options to explain a substantial change in oxygen isotopes such as observed for Kluchevskoy lavas are (1) crustal assimilation, (2) source contamination by subducted sediments or (3) involvement of fluids from the altered oceanic crust. These possibilities are further evaluated in the following chapters.

Crustal Assimilation

Assimilation of crust is widely accepted as major cause of the ^{18}O -enrichment in volcanic rocks for various continental arcs (e.g. Harmon and Hoefs, 1995; James, 1981; Taylor, 1980). Even OIB's, erupting through thin oceanic crust can be strongly contaminated by altered basalts (Eiler et al., 1997a; Eiler et al., 1996; Harris et al., 1999). Unlike in arc environments OIB tend to show depleted $\delta^{18}\text{O}$ values, suggesting a role for high-T altered rocks in their origin. Assimilation of low-T altered crust therefore needs to be tested as a possibility to explain the ^{18}O -enriched Kluchevskoy lavas.

The crust below the CKD consists of Cretaceous and Tertiary accreted arc and oceanic material (Khrenov et al., 1991). Such young volcanic rocks or volcanoclastic sediments will be close to mantle values in Pb and Nd isotope composition. Sr and oxygen isotopic compositions, however, may be more variable, because of low-T exchange with seawater. Dobson and O'Neil (1987) report $\delta^{18}\text{O}$ values up to 15 ‰ for dacitic rocks from Bonin Islands, whereas pyroxene phenocrysts of the same rocks give mantle values. Obviously, arc rocks erupting into a submarine environment can also become ^{18}O -enriched by seawater alteration similar to oceanic crust. In Fig. 3-8 we used an AFC model to produce the steep trends between $\delta^{18}\text{O}$ and Sr by crustal assimilation (end-members used in the AFC and the mixing models are combined in Tab. 3-4). The rate of assimilation of arc crust and crystallization (r) is assumed to be no larger than 0.5. If a MORB-type composition with $\delta^{18}\text{O}=5.7$ ‰ and $^{87}\text{Sr}/^{86}\text{Sr}=0.7028$ (Ito et al., 1987) is used for the mantle derived magma, the steep trend between Sr and O-isotopes cannot be reproduced by the model. The observed trend can be modeled only when assuming an enriched source, contaminated with sediment or fluid from the slab (see Fig. 3-9).

However, several reasons argue against such model. To produce the most ^{18}O -enriched HAB, the mantle-derived magma has to be extensively fractionated. The data range between $F=0.9$ and $F=0.65$ for the different AFC curves. This results in a calculated proportion of 10 to 23 % assimilated altered mafic crust. At this proportion,

the assimilant forms up to 45 % of the resulting magma. Even the most primitive sample KLU-16 with $\delta^{18}\text{O}=6.4\text{‰}$ would need $>20\%$ fractionation and $>10\%$ assimilation, which is not consistent with its primitive Mg# number of 71. An AFC process should also strongly increase the contents of SiO_2 and all incompatible trace elements. The AFC model would only work, if the assimilant was basaltic in composition. However from thermal balance, it is impossible for a basaltic magma to assimilate large volumes of basaltic wall rock.

Alternatively we consider AFC with a sedimentary crustal component. The dashed model curve in Fig. 3-8B falls close to the data array in the Sr-O isotope diagram and would suggest 4-12 % of sediment assimilation to explain the high oxygen isotope ratios of the magmas. However, for several other parameters (e.g. Sr versus oxygen isotopes in Fig. 3-8A) such high contribution from sediments is untenable (Bailey, 1996; Kersting and Arculus, 1995; Tsvetkov et al., 1991; Turner et al., 1998).

We conclude, although fractional crystallization has effected the bulk rock composition, assimilation of Kluchevskoy magmas by crustal rocks cannot explain the observed high oxygen isotope ratios and Sr-O-isotope trend.

Source contamination by sediments

It is well established by $^{207}\text{Pb}/^{204}\text{Pb}$, $^{10}\text{Be}/\text{Be}$, or $\delta^{11}\text{B}$ composition in arc rocks that sediments contribute to arc volcanism (e.g. Brown et al., 1982; Ishikawa and Tera, 1997; White and Dupre, 1986). Sediments have also the potential to enrich the mantle in $\delta^{18}\text{O}$. Northwest Pacific sediments are rich in siliceous ooze and reach $\delta^{18}\text{O}$ values of up to 30 ‰ (Rea, 1993). At subduction, fluids or melts derived from such sediments might introduce an ^{18}O -rich component into the mantle source. In order to test the role of a sediment component, we calculated simple binary mixing models using oceanic sediments with $^{87}\text{Sr}/^{86}\text{Sr}=0.707$ and $\delta^{18}\text{O}=20\text{‰}$. The Sr concentration was derived from Bailey (1996) and the $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}$ are assumed to be in equilibrium with Cretaceous seawater. The model (3-. 9 A and B) shows that even a minor sediment contribution to the mantle source would drastically change Sr, Nd, and Pb isotope ratios without any significant change in $\delta^{18}\text{O}$. Based on our data, the maximum possible sedimentary contribution to the Kluchevskoy lavas is about 1 %. This estimate is consistent with earlier studies by Bailey (1996), Kersting and Arculus (1995), Tsvetkov et al. (1991) and Turner et al. (1998) based on radiogenic isotopes and trace element ratios. Calculations with melts or fluids derived from subducted sediments and mixed into the mantle wedge source give similar results. Simply adding a sedimentary component to the Kluchevskoy magma source is clearly ruled out to explain the ^{18}O -enrichment.

Source contamination by fluids from the altered oceanic crust

The upper oceanic crust is ^{18}O -enriched by hydrothermal precipitation of hydrous minerals from seawater and seafloor weathering, as documented from studies of ODP drill cores and obducted ancient oceanic crust (e.g. Staudigel et al., 1996; Wenner and Taylor, 1974). Little change of the original Nd and Pb isotope composition of MORB occur by hydrothermal processes or seafloor weathering due to low Nd and Pb abundances in seawater. The upper oceanic crust is further characterized by ^{87}Sr enrichment, which has been shown to be strongly correlated with $\delta^{18}\text{O}$ values (Staudigel et al., 1996). However, this correlation is based on samples from a single location in the Atlantic. The correlation mainly depends on the Sr isotopic composition of the ocean water in the first few Ma after ocean crust formation. Additional variations also can be expected for the Pacific MORB, which is more unradiogenic in Sr than the Atlantic MORB (Ito et al., 1987). From these considerations a maximum of 12 ‰ is assumed for the low-T altered oceanic crust. Involvement of such ^{18}O -enriched crust in the magma source appears to be more consistent with the isotopic signatures of Kluchevskoy lavas. However, direct melting of subducted oceanic crust must be excluded because Kluchevskoy lavas are far from adakitic in their major and trace element compositions (Drummond et al., 1996).

Aqueous fluids can be released by the breakdown of hydrous minerals from the slab down to more than 100 km. It was shown experimentally by Brenan et al. (1995b) and Stalder et al. (1998) that such fluids are enriched in alkalis, alkaline earths, U, Th, and Pb but essentially free of HFSE and HREE. The large contrast in Sr concentration between slab-derived fluids (550ppm Sr after Brenan et al., 1995b) and depleted mantle (16.6 ppm Sr after McCulloch and Bennett, 1994)) results in a large leverage of the fluid on the mantle Sr isotope composition, while the oxygen isotope composition is not changed much. This causes a steep trend between Sr and O-isotopes as mixtures between a MORB-type mantle and fluids derived from subducted oceanic crust. Fig. 3-9 shows such steep mixing trends between a depleted/enriched mantle source and a slab fluid of 12 ‰. The calculated trends fall close to the observed compositions, however the amount of fluid in the source with 5-20 wt% is rather high. Such large amounts of hydrous fluid would cause extensive and unrealistically high melting (Stolper and Newman, 1994). Pineau et al. (1999) argued for Kamchatka that the ^{18}O -rich component shall be a hydrous melt rather than a hydrous fluid. However hydrous melts are quite different in trace elements to hydrous fluids, particularly in the absence of the HFSE depletion (Brenan et al., 1995b). From trace element pattern of Kluchevskoy samples no evidence exist for a hydrous melt component.

A simple mixing between fluids and the mantle is therefore ruled out to explain the source of the ^{18}O -enriched Kluchevskoy samples.

An $\delta^{18}\text{O}$ -enriched mantle wedge?

In the previous chapter we calculated a mixture between the mantle and a slab-derived fluid, with the result of unrealistic high amounts of fluid in the magma source. However, if we allow for time, the amount of infiltrating fluid at any given stage can be much less than that estimate for the bulk rock/water ratio. In the next chapters we want to explain and discuss the following model:

- 1) Small amounts of hydrous ^{18}O -enriched fluid, are liberated from the slab and migrate into the overlying non-convecting and cold lithospheric part of the mantle wedge over some Ma.
- 2) The fluid forms hydrous minerals in the mantle. Its kind and quantity depends on the P-T-conditions in the mantle wedge and the chemical composition (i.e. availability of K, Na, Al) of the mantle and fluid. Only a small amount of fluid will be instantly fixed in hydrous phases, the remaining part will migrate deeper into the mantle until is completely reacted.
- 3) Equilibration with mantle mineralogy and the newly formed hydrous minerals will result in a concentration profile of ^{18}O and certain trace elements from the slab into the mantle. In an extreme case the mantle close to the slab is completely equilibrated with the slab fluid and the fluid far away from the slab is completely equilibrated with the mantle minerals. The composition of the mantle and fluid between these two extreme cases can be modeled by percolation (Navon and Stolper, 1987) or zone refining models (Ayers, 1998). To simplify the model, we only want to discuss the end member compositions, which prove qualitatively that the co-variations of trace elements and radiogenic isotopes with $\delta^{18}\text{O}$ can be produced in the source.
- 4) Such metasomatized mantle may presently become involved in arc magmatism due to intra-arc rifting of the CKD. Melting and maybe mixing of the differently metasomatized mantle regions will create the observed correlations with $\delta^{18}\text{O}$.

Slab fluid composition

A critical parameter in our model is the composition of the infiltrating slab fluid, which depends on pressure, temperature, mineralogical and chemical composition of the slab. The P-T conditions in the uppermost part of the slab in the region underlying the non-convecting lithospheric mantle (30-90km) can be estimated using the

modeling of Peacock (1993). The situation for Kamchatka is similar to the Aleutians, i.e. fast subduction of an old slab, which results in a relatively cold P-T path ($T=200\text{--}600^\circ\text{C}$ at 1-3 GPa and for moderate shear heating). At these conditions the fluid should be a hydrous fluid rather than a hydrous melt. Problems arise because all studies, which have examined the capacity of hydrous fluids to concentrate and transport trace elements in a slab environment were performed at temperatures exceeding 900°C . An extrapolation of these results to lower temperatures may be inappropriate. Fluid/mineral partition data are only available for those phases which are restricted to the deeper part of the slab, such as garnet, clinopyroxene, amphibole, rutile, orthopyroxene and olivine (Adam et al., 1997; Ayers, 1998; Brenan et al., 1995b; Stalder et al., 1998). Fluid/mineral partition behavior for other phases like apatite, lawsonite, chlorite, chloritoid, epidote, zoisite-clinozoisite, phengite and serpentine which are likely residual phases in shallower regions (see Schmidt and Poli, 1998 and references there) are unknown. However even minor amounts of these phases can strongly influence the trace element partitioning. K, Rb, Ba and Cs are carried essentially by phengite (Sorensen et al., 1997), Y and REE by lawsonite and apatite (Tribuzio et al., 1996). A more reliable estimate of the fluid composition can be derived from studies of high-pressure metamorphic terranes (Bebout, 1995; Sorensen et al., 1997). From these, at least the general suggestion about the composition of a shallow slab fluid can be made, that they will be enriched in LILE and LREE but poor in HREE and HFSE similar to the deeper-derived fluids. Comparing the trace element patterns for Kluchevskoy with other rocks of the CKD and EVF (Fig. 3-3), it is obvious that the patterns are similar and argue for relatively similar composed fluid components involved. Therefore the slab fluid composition was calculated from $D_{\text{mineral/fluid}}$ data for 2-3 GPa and $900\text{--}1100^\circ\text{C}$ of Ayers (1998) and Brenan et al. (1995b) assuming 1 % fluid dehydration from an eclogite composed of 40 % clinopyroxene, 59 % garnet and 1 % rutile. This assumptions are identical to these made by Brenan et al. (1995b). Because of the limited number of analyzed elements in the altered MORB composition of McCulloch and Gamble (1991) we used the estimate of Staudigel et al. (1996).

The $\delta^{18}\text{O}$ of the altered MORB was discussed in a previous chapter to be around 12 ‰. Some fractionation may occur between the fluid and the eclogitic residue (Zheng, 1993b). However, determinations of $\delta^{18}\text{O}$ in precipitates from slab fluids in obducted rock units (Bebout and Barton, 1993) and measurements of $\delta^{18}\text{O}$ in water-rich melt inclusions (Eiler et al., 1998) gave comparable values for the slab fluid.

Mantle composition

The Nb_N/Yb_N ratios of Kluchevskoy samples show, that its magma source was similar or even slightly more depleted than the MORB source (Fig. 3-3). From the Sr and O-isotope variation it is likely, that this source was contaminated by some limited amounts of sediment (<1%). In our model we calculated the source (EM) as a mixture of depleted mantle (DM) and 0.5 % of sediment (Tab 3-5). The use of DM without sediment addition in the calculation decreases the element concentrations in the wedge equilibrated fluid but does not much change the results of the model.

Constraints on fluid-mantle interaction

Fluids derived from the slab will percolate on grain boundaries or shear zones into the mantle wedge and react immediately with mantle minerals to hydrous phases like serpentine, chlorite, talc, amphibole or phlogopite depending on their P-T-stability (see Schmidt and Poli (1998) and references there). If no further mantle minerals can be reacted, new batches of fluid will migrate in unreacted mantle regions.

Serpentine is a potential mineral of the hydrated mantle, which was shown to be stable until 720°C at 2 GPa (Ulmer and Trommsdorff, 1995), i.e. conditions which occur in the upper part of the lithospheric mantle and close to the slab interface. Xenoliths, which show evidence of serpentinization were described rarely to occur in Kamchatka volcanics (Erlich and Gorshkov, 1979; Shcheka, 1976). However, a serpentinized mantle region could not yet detected by geophysical studies. Serpentine, and similarly talc and chlorite can play a major role in the depletion of ¹⁸O in the fluid but have no influence on the trace element variations because of their very low mineral-fluid partition coefficients ($D_{\text{mineral/fluid}}$).

The only phases with high $D_{\text{mineral/fluid}}$ for fluid mobile elements, which are stable in a hydrated mantle, are amphibole (shallower than 70 km) and phlogopite. From the available amount of Al, K and Na in a depleted mantle about 10-15 % amphibole but not significantly phlogopite can be formed. Alkalis are highly enriched in the slab fluid. The fluid introduced K-metasomatism results in the formation of some percent phlogopite closely to the slab or in veins, which serve as pathway for the fluid. Evidence for this process comes from mantle xenoliths, which often contain disseminated amphibole and phlogopite up to some percent but also small veins entirely formed by them (Ionov et al. (1997) and references therein). The water content of a hydrated mantle with 10 % amphibole and some phlogopite will be 0.2 to 0.3 %. It is increased up to 6 %, if chlorite, talc or serpentine are additional stable phases (Schmidt and Poli, 1998).

Elemental variations with $\delta^{18}\text{O}$

Oxygen isotopes and fluid-mobile trace elements will behave quite differently and form distinct gradients in the fluid percolation process from the slab into the mantle wedge. Because oxygen is the major component of the mantle and the fluid and all newly formed hydrous phases oxygen isotopes of the fluid will equilibrate with the mantle after a short migration distance. As result there will be a relatively steep concentration profile for ^{18}O from the slab into the mantle.

The trace element content of the fluid, which migrates through the mantle wedge depends on the initial slab fluid composition and the extend of exchange with mantle minerals including newly formed hydrous minerals which can cause an enrichment or depletion of different elements. This should lead to a concentration profile of certain trace elements in the mantle wedge and related variations in $\delta^{18}\text{O}$. The final fluid composition will then be controlled by, and can be calculated from partition coefficients between the mantle and the fluid. Ayers (1998) has argued, that the trace element enrichment for primitive island arc magmas can in principle be derived by mixing of the mantle with such mantle equilibrated fluid. Such wedge fluid is calculated from $D_{\text{mineral/fluid}}$ from Ayers (1998) and Brenan et al. (1995b). Missing data for $D_{\text{mineral/fluid}}$ in amphibole and orthopyroxene were calculated from their $D_{\text{cpx/fluid}}$ data, combined with $D_{\text{cpx/melt}}$, $D_{\text{amph/melt}}$ and $D_{\text{opx/melt}}$ data from Foley et al. (1996), Hart and Dunn (1993), Hauri et al. (1994), Kennedy et al. (1993), LaTourrette et al. (1995) and Zack (1997). The model-mantle contains 60 % olivine, 30 % orthopyroxene, and 10 % amphibole, its composition is shown in Tab 3-5. The limited availability of $D_{\text{mineral/fluid}}$ restricts the considered elements to Rb, Ba, Th, U, Pb, Sr, Nb, Zr, Y, La, Sm and Tm (missing D_{Tm} calculated from $D_{\text{Tm}}=(D_{\text{Er}}+D_{\text{Yb}})/2$).

The two distinct fluids (Tab 3-5) interact with, and create two different magma sources in the mantle wedge. The degree of mantle enrichment or depletion of a fluid-mobile element by the migrating fluid is described by the ratio between the concentration of that element in the slab-equilibrated fluid (C_{SF}) and the concentration in the wedge equilibrated fluid (C_{WF}). If $C_{\text{SF}} > C_{\text{WF}}$, the trace element content will decrease with the distance to the slab. These elements should positively correlate with $\delta^{18}\text{O}$. By contrast, those elements with $C_{\text{SF}} < C_{\text{WF}}$ will be depleted by the fluid in the mantle and should be negatively correlated with $\delta^{18}\text{O}$.

Fluid-mobile elements

From $C_{SF} > C_{WF}$ (Tab 3-5) enrichments can be predicted for Ba, Sr, Rb, La, Th, U and Pb in the slab-fluid modified mantle which (at 5 to 20 % fluid interaction) also has the appropriate ^{18}O -enriched isotope composition. Mixing magmas from these sources or mixing the distinct mantle domains before melting will cause the observed positive correlations between $\delta^{18}\text{O}$ and slab-fluid enriched elements. Our model predicts that Rb and Ba, which have the highest C_{SF}/C_{WF} ratio, should be particularly well correlated with $\delta^{18}\text{O}$. This is in fact what is observed (Tab 3-2, Fig. 3-5). Additional phlogopite in the wedge would even increase the C_{SF}/C_{WF} ratio for Rb and Ba because phlogopite retains these elements from the fluid. Additional evidence for a preferential depletion of Rb, Ba (and K) in the fluid comes from positive correlations of ratios of K, Ba and Rb with all other fluid-mobile elements versus $\delta^{18}\text{O}$ (shown by the Ba/Sr ratio in Fig. 3-7).

Pb is generally considered to be a highly fluid mobile element (Brenan et al., 1995a) and therefore the weak correlation with $\delta^{18}\text{O}$ is unexpected. However this contradiction exist only on the first view. All mantle minerals including amphibole have very low $D_{\text{mineral/fluid}}$ values for Pb. Therefore the fluid gets not much depleted in Pb, which means that no Pb enrichment of the mantle minerals occur. This explains that Pb correlates only weakly with $\delta^{18}\text{O}$.

The U/Th ratio of the fluid migrating through the mantle is increased because Th is more compatible in clinopyroxene than U (Brenan et al., 1995b). Garnet would cause the opposite, which suggests, that garnet is not a stable phase in this part of the mantle. The relatively high U/Th ratio for Kluchevskoy compared to other volcanics of Kamchatka (Churikova et al., 2000; Turner et al., 1998) can be an indication, that melts derived from a strongly metasomatized mantle dominate for Kluchevskoy.

Melt mobile elements

The HFSE (Nb, Zr), Y and all REE except La have $C_{SF} < C_{WF}$ that lead to a relative enrichment in the wedge fluid combined with mantle depletion in these elements. However the difference is not large and their concentration should stay at a constant level with little changes in the parameters of the model (higher depleted mantle wedge, larger concentrations of HFSE and REE in the slab fluid).

Garnet, which has a major influence on the LREE/HREE fractionation is widespread in the slab but rare or absent in the mantle wedge. This cause the four times higher La/Tm ratio in the calculated slab fluid compared to the wedge fluid and corresponds to the observed positive correlation of LREE/HREE ratios with $\delta^{18}\text{O}$ Fig. 3-7).

Sr, Pb and Nd isotopes

Beside the C_{SF}/C_{WF} ratio, which determines the element enrichment or depletion of certain elements in the wedge, isotopic ratios additionally depend from the ratio between the element content in the slab fluid and the unmetasomatized mantle. This is because isotopic ratios are changed by exchange with mantle minerals. The isotope ratio of metasomatized mantle can be calculated as simple mixture between the slab fluid and the mantle in the ideal case of a total equilibrium (like in Fig. 3-9B). The slab introduced isotopic anomaly will travel further than expected from mixing calculations for non-equilibrium conditions. This behavior is not only valid for radiogenic isotopes but also for stable isotopes like oxygen.

Sr and Pb contents are low in the mantle but have high concentrations in both calculated fluids. Therefore the Sr and Pb isotope ratios of the metasomatized mantle will be largely controlled by the isotope composition of the slab. $^{87}\text{Sr}/^{86}\text{Sr}$ and Pb isotopic ratios show almost no co-variations with $\delta^{18}\text{O}$ in Kluchevskoy samples. Interestingly the field for Pb isotopes from Kluchevskoy and for whole Kamchatka overlaps with the fields of the Hawaii plume (Fig. 3-4). No Pb isotope data exist from the Obruchev ridge, the northern termination of the Hawaii-Emperor seamount chain. If we assume, that the Hawaiian plume component has not significantly changed isotopically in Pb over the last 100 Ma, we can explain the Pb isotopic ratios in the Kluchevskoy rocks to be largely derived from fluids of this altered plume material.

Nd will behave similar to Sm, which has low concentrations in the slab fluid compared to the mantle. Therefore the Nd isotope ratio will be defined almost entirely by the wedge and a correlation with $\delta^{18}\text{O}$ is not expected, corresponding to what is observed in our data.

Constraints on the time for source enrichment from $^{232}\text{U}/^{230}\text{Th}$ disequilibrium, $^{10}\text{Be}/\text{Be}$, Rb-Sr and a mass balance for H_2O in the slab

Turner and Hawkesworth (1997) have shown convincingly, that transfer times for sediment signals from the slab to the melting region may be in the order of a few Ma. Time elapsed between fluid enrichment in the arc magma source is in the order of 30.000 to >150.000 a (Elliott et al., 1997; Turner and Hawkesworth, 1997; Turner et al., 1998). Following our model, the increase of the U/Th ratio, connected with the depletion in ^{18}O , should be expressed in a strong U-Th isotope disequilibrium, provided this enrichment process is younger than 300.000 years. However, observed $^{232}\text{U}/^{230}\text{Th}$ disequilibrium is weak or absent (1.0-1.1) and there is no correlation with $\delta^{18}\text{O}$ (Fig. 3-7). In addition, overall U/Th ratios in Kluchevskoy samples are considerable higher than we would expect from depleted mantle-derived melts. This

implies, that the process of U over Th enrichment was lost by isotopic decay and ^{230}Th ingrowths. Therefore, the U enrichment, and by implication the enrichment of all other fluid-mobile elements, must have occurred in the mantle wedge more than 300.000 years ago.

It was shown that a maximum of 1 % sediment is possible in the source. Even 1 % of sediment in the source can create detectable ^{10}Be enrichment (Ryan and Langmuir, 1988). However $^{10}\text{Be}/\text{Be}$ ratio was found to be extremely low for a Kluchevskoy sample as well compared with other samples of Kamchatka and other arcs (Tsvetkov et al., 1991). Therefore if we assume that some limited amounts of sediment were introduced in the source, the time after enrichment had exceed several Ma resulting in an complete radioactive decay of ^{10}Be .

The differences between the differently ^{18}O -enriched mantle sources in Rb/Sr (0.03-0.05, assuming the Rb/Sr ratio is not much changed by melting) will cause a change in the isotopic composition of Sr and Pb with time. Rb/Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ are relatively well correlated, and give a reference isochrone of 150 ± 80 Ma. This calculation assumes an enriched mantle source with different Rb/Sr but similar $^{87}\text{Sr}/^{86}\text{Sr}$. However, different extends of interaction between a slab fluid with high Rb/Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ and the mantle create a similar trend. Therefore the age of 150 ± 80 Ma express an upper time limit for mantle metasomatism.

A simple mass balance shows, shall show, which time was necessary to create the ^{18}O -enriched source. Schmidt and Poli (1998) argued that a complete serpentinization and chloritization of most part of the lithospheric part of the wedge is achieved after subduction of 570-790 km slab (30° subduction angle). For Kamchatka with a subduction rate of 9 cm/a, such hydrated mantle (with 6 % H_2O) will be created in less than 10 Ma. It is not beyond the scope of this paper to speculate about the water content or thermal stability of hydrous minerals in such mantle. However, the large flux of water from the slab into the lithospheric mantle must result in a far-reaching metasomatism with a coupled ^{18}O -enrichment.

Special conditions for Kluchevskoy?

What is so special about Kluchevskoy volcano that the process of lithospheric ^{18}O -enrichment by slab fluids can be detected only here?

1) Neither slab dehydration at shallow levels prior to melting nor ^{18}O -enriched fluids in subducted oceanic crust should be unique to Kamchatka. Is there a higher fluid flux? A special feature of subduction below the Kluchevskaya Group is the subduction of the Emperor seamount chain, one of the largest of its kind on the globe. This chain is composed essentially by low-T hydrothermal altered pillow lavas and

volcaniclastics. Fast subduction of the relatively old and cold Pacific plate then favors the flux of much of this ^{18}O -enriched water into deeper parts of the mantle (Peacock, 1993). A consequence of this is the extremely large magma production rate (the largest in any arc) and the extremely wide extension of active volcanic activity over the arc (~200km) just where the seamount chain is subducted. It therefore seems plausible that these special circumstances, which all involve an increased role of slab-derived fluids may be ultimately related to the observed unusual ^{18}O -enriched compositions.

2) Sediments seems to play a neglectable role (Sr and Pb isotopes) and extensive crustal contamination processes are limited for these mafic rocks. Therefore it should be easier to trace the process of wedge enrichment for Kamchatka than in other arcs on thick continental crust or with significant sediment subduction. The ^{18}O -enrichment is not only restricted on Kluchevskoy volcano but is also found in other centers of the CKD and EVF. The back arc Ichinsky volcano, however, erupted magmas close to mantle values in $\delta^{18}\text{O}$ (unpublished data of the authors).

3) In most arcs systems metasomatized lithospheric mantle contribute only subordinately to magmatism and the magma is mostly derived from the convecting wedge. On Kamchatka the intra-arc rifting of the CKD cause that such mantle regions presently become involved in arc magmatism. Either it forms partial melts, caused by the raising of the thermal gradient or it is assimilated by melts from the asthenospheric mantle.

Conclusions

Oxygen isotope ratios of olivines and clinopyroxenes from the Kluchevskoy volcano provide distinctly higher values than for MORB. Because assimilation of significant arc crust is ruled out, the source is considered to be different from the MORB-type mantle. Strong positive correlations between $\delta^{18}\text{O}$ and fluid mobile major (K, Si) and trace elements (Cs, Li, Sr, Rb, Ba, Th, U, LREE) argue for alteration of a depleted mantle by hydrous fluids. Sr and Pb are mainly fluid derived and their isotopic compositions can be taken as signature of the altered MORB or OIB type component. Mass balance calculations allow not more than 1 % sediments involved in the melting process. However, the similarities between Kluchevskoy rocks and the Hawaii plume component in Pb isotopic compositions prove that no additionally sediment is necessary to explain the slight radiogenic enrichment compared to MORB.

The large amount of fluid needed argues against a simple fluid-induced melting. Melting and fluid transfer from the slab has to be de-coupled in time and space. Based on a fluid infiltration model, an enrichment of the nonconvecting sub-arc lithosphere over at least 10 Ma is necessary to produce a sufficiently ^{18}O -enriched mantle volume. Melts from different regions will inherit these trends. Negative correlation of $\delta^{18}\text{O}$ with U/Th suggest that U is more mobile than Th in the mantle wedge, supporting the idea that U/Th disequilibrium forms by reaction of water-rich fluids with mantle minerals. Element correlations with $\delta^{18}\text{O}$ argue for a lithospheric mantle, containing amphibole and maybe phlogopite but free of garnet.

Steep correlations of $\delta^{18}\text{O}$ with $^{87}\text{Sr}/^{86}\text{Sr}$ and correlations between $\delta^{18}\text{O}$ and SiO_2 or K_2O in the Japan arc and the Andes (Taylor, 1986), until now explained by crustal assimilation, can also be the result of such longtime fluid-mantle interaction. The further extension of the laser fluorination method for oxygen isotope studies in other arcs will soon enlarge our knowledge and understanding of the flux of water between mantle and crust, which is still a matter of current debate (Ito and Anderson, 1983; Peacock, 1990; Schmidt and Poli, 1998).

Tab. 3-1

Major element data for samples from Kluchevskoy volcano. Correlation coefficients and standard deviations were determined for major elements (normalized to a volatile free sum of 100%) versus ^{18}O . A strong covariation can be assumed if both correlation coefficient and standard deviation are high. Significant correlations ($r > 0.6$ or $r < -0.6$) and relative standard deviations larger 10 are stressed by bold numbers. The normalization procedure to Mg#70, performed to correct for mineral fractionation, is described in detail in the text.

Sample	Locality*	Age*	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	H ₂ O	Mg#**
KLU-01	cone Bilyukai (flow)	1938	53.71	0.94	15.86	8.53	0.17	7.32	9.38	2.95	0.94	0.18	0.23	60.5
KLU-02	cone Bylinkina (bomb)	1951	53.99	1.11	18.06	8.27	0.16	5.19	8.21	3.61	1.18	0.22	0.16	52.8
KLU-03	waterfall E of crater Oehki (flow)	4 -1500 b.p.	53.49	0.85	15.27	8.24	0.16	8.84	9.36	2.88	0.76	0.16	0.11	65.7
KLU-04	N of cone Srezanny (flow)	4 -1500 b.p.	52.50	1.08	16.08	8.92	0.17	7.74	9.44	3.15	0.71	0.19	0.19	60.7
KLU-05	N of cone Srezanny (flow)	4 -1500 b.p.	52.71	0.99	16.42	8.61	0.16	7.52	9.41	3.19	0.79	0.19	0.33	60.9
KLU-06	cone Srezanny (bomb)	4 -1500 b.p.	53.44	0.89	15.23	8.51	0.16	8.32	9.69	2.84	0.76	0.16	0.13	63.5
KLU-07	cone Bokovoi (bomb)	4 -1500 b.p.	53.50	0.84	14.59	8.21	0.16	9.44	9.59	2.78	0.74	0.15	0.30	67.2
KLU-08	cone "K"/Red cone (bomb)	4 -1500 b.p.	52.76	1.00	16.62	8.53	0.16	7.41	9.39	3.14	0.80	0.20	0.32	60.8
KLU-09	cone "M" (bomb)	4 -1500 b.p.	52.74	0.97	15.56	8.73	0.17	8.32	9.72	2.98	0.66	0.17	0.31	62.9
KLU-10	waterfall S of cone "M" (flow)	4 -1500 b.p.	52.72	0.98	15.75	8.73	0.17	8.22	9.74	2.88	0.65	0.17	0.25	62.7
KLU-11	waterfall S of cone "M" (flow)	4 -1500 b.p.	52.49	0.96	15.79	8.85	0.17	8.21	9.77	2.96	0.63	0.16	0.30	62.3
KLU-12	cone Bylinkina (flow)	1951	54.14	1.11	18.13	8.24	0.16	5.04	8.16	3.61	1.19	0.22	0.28	52.2
KLU-13	cone Belyankin (flow)	1953	54.25	1.13	18.54	8.25	0.16	4.61	8.02	3.60	1.20	0.23	0.17	49.9
KLU-14	cone Vernadsky (flow)	1956	54.44	1.11	17.90	8.36	0.17	4.95	8.20	3.48	1.17	0.22	0.19	51.4
KLU-15	cone Tuyta (flow)	1932	53.49	0.86	14.62	8.29	0.17	8.68	10.05	2.74	0.91	0.17	0.31	65.1
KLU-16	cone Bulochka (flow)	4 -1500 b.p.	51.94	0.81	13.36	8.68	0.18	11.72	10.23	2.39	0.56	0.13		70.6
Correlation coefficient (r)			0.90	0.37	0.53	-0.76	-0.39	-0.63	-0.69	0.53	0.90	0.59	-0.21	-0.63
Correlation after normalisation to Mg#70 (r ₇₀)			0.57	0.12	-0.02	-0.55	-0.16	-0.55	-0.57	0.21	0.96	0.56	-0.27	-
Standard deviation in % ()			1	11	9	3	3	24	7	11	25	16	41	9
Standard deviation in % after normalisation to Mg#70 (r ₇₀)			1	5	2	2	2	2	3	3	17	7	44	-

* The notation of the localities and ages are based on Khrenov et al. (1991) and an unpublished map of Ermakov (1968)

** Mg# = Mg/(Mg+Fe_{ox})*100

Tab. 3-2

Trace element data for samples from Kluchevskoy volcano (trace elements measured by ICPMS, except for Ba, Co, Cr, Ga, Ni, Sc, Sr, V, Zn and Zr which were measured by XRF). Regression coefficients for trace elements versus $\delta^{18}\text{O}$ and standard deviations of the elements of the raw data and fractionation corrected data are shown additionally. Strong correlations ($r > 0.6$ and $r < -0.6$) and relative standard deviations $1.5\times$ larger than the analytical error are stressed by bold numbers.

	KLU-01	KLU-02	KLU-03	KLU-04	KLU-05	KLU-06	KLU-07	KLU-08	KLU-09	KLU-10	KLU-11	KLU-12	KLU-13	KLU-14	KLU-15	KLU-16	r	r ⁷⁰	σ	σ^{70}
Li	10.9	13.2	8.3	7.8	9.1	8.1	8.6	8.9	8.3	7.5	7.9	13.9	13.3	13.5	9.8		0.86	0.89	23	17
Be	0.55	0.63	0.50	0.58	0.62	0.48	0.47	0.62	0.50	0.49	0.54	0.66	0.68	0.71	0.51		0.48	0.29	13	7
Sc	33.0	29.9	35.9	35.2	35.1	34.0	36.0	30.9	35.0	35.1	36.9	21.1	27.0	27.1	38.1	41.5	-0.60	-0.03	15	5
V	255	259	239	249	235	245	244	246	250	256	261	260	267	259	246	244	0.47	0.21	3	2
Cr	256	45	424	285	241	341	500	220	343	319	320	31	6	33	432	857	-0.52	-0.16	72	6
Co	32.0	36.9	36.9	39.2	39.2	40.0	40.0	34.9	38.0	39.1	35.9	33.1	30.0	33.1	40.1	47.6	-0.54	-0.16	11	4
Ni	93	39	150	100	106	107	166	88	104	108	109	31	14	21	110	206	-0.62	0.04	52	6
Cu	79	84	60	79	74	59	64	72	78	74	73	91	88	83	77		0.49	0.27	12	8
Zn	85	88	79	84	80	81	78	80	78	81	81	87	88	89	77	56	0.47	0.24	9	6
Ga	19.0	17.9	15.9	15.1	18.1	16.0	16.0	17.0	17.0	19.0	18.0	18.0	19.0	18.0	15.0	15.2	0.24	-0.18	8	5
Rb	15.1	17.8	12.2	10.2	12.3	11.3	11.6	11.9	9.5	9.4	9.4	19.0	19.0	19.3	15.8		0.94	0.95	27	21
Sr	341	392	323	295	316	299	312	318	290	291	286	398	403	375	334	246	0.85	0.81	13	8
Y	18.5	21.2	14.9	19.5	17.9	15.9	15.3	18.5	17.8	18.3	19.0	22.0	21.8	23.1	17.6	67	0.50	0.40	13	7
Zr	87	104	81	101	99	81	77	98	87	85	85	104	105	107	75		0.35	-0.05	13	6
Nb	1.46	1.75	1.15	1.70	1.67	1.17	1.31	1.78	1.43	1.46	1.39	1.99	1.92	2.00	1.30		0.37	0.16	18	11
Cs	0.43	0.47	0.42	0.36	0.46	0.28	0.39	0.39	0.33	0.31	0.32	0.51	0.48	0.58	0.44		0.72	0.63	20	16
Ba	344	396	289	224	260	283	280	260	243	224	228	435	428	403	308	229	0.92	0.93	24	18
La	6.09	7.55	5.41	6.12	6.69	5.03	5.31	6.72	5.54	5.32	5.36	8.43	8.20	8.42	6.80		0.71	0.70	18	12
Ce	15.1	19.3	13.6	16.3	17.1	13.0	13.1	17.5	14.2	14.2	14.6	21.1	21.3	21.5	17.0		0.65	0.63	17	11
Pr	2.49	3.16	2.17	2.62	2.77	2.14	2.13	2.83	2.38	2.34	2.46	3.39	3.54	3.61	2.71		0.64	0.63	18	11
Nd	11.9	14.9	10.4	12.4	12.7	10.2	10.3	12.9	11.2	11.4	11.6	15.8	15.6	16.7	12.3		0.64	0.65	16	9
Sm	3.35	4.07	2.94	3.54	3.41	2.91	2.99	3.50	3.07	3.21	3.25	4.14	4.11	4.27	3.36		0.64	0.65	13	7
Eu	1.06	1.26	0.90	1.07	1.04	0.94	0.93	1.07	1.01	1.02	0.97	1.27	1.29	1.33	1.02		0.66	0.72	12	6
Gd	3.32	3.75	2.89	3.52	3.35	3.01	2.87	3.35	3.18	3.20	3.20	3.77	3.76	3.88	3.04		0.50	0.36	10	3
Tb	0.54	0.62	0.45	0.57	0.54	0.48	0.46	0.56	0.53	0.55	0.56	0.63	0.65	0.64	0.51		0.44	0.24	11	5
Dy	3.42	3.82	2.87	3.66	3.27	3.07	2.91	3.46	3.36	3.42	3.42	3.84	3.82	4.04	3.05		0.39	0.12	10	4
Ho	0.71	0.77	0.61	0.79	0.69	0.64	0.59	0.71	0.68	0.70	0.70	0.82	0.81	0.83	0.66		0.43	0.21	10	5
Er	1.99	2.22	1.68	2.27	1.98	1.82	1.73	2.06	1.95	2.06	2.04	2.36	2.34	2.38	1.84		0.35	0.05	11	5
Tm	0.29	0.33	0.26	0.33	0.30	0.27	0.25	0.30	0.28	0.31	0.31	0.34	0.36	0.34	0.28		0.38	0.10	10	5
Yb	1.94	2.13	1.61	2.10	1.91	1.67	1.61	1.98	1.84	1.98	1.96	2.15	2.16	2.26	1.69		0.30	-0.04	11	5
Lu	0.29	0.34	0.25	0.32	0.29	0.25	0.24	0.30	0.29	0.30	0.30	0.34	0.32	0.33	0.26		0.23	-0.16	11	6
Hf	2.04	2.49	1.88	2.35	2.25	1.98	1.86	2.32	2.08	2.07	2.03	2.55	2.56	2.57	1.89		0.41	0.15	12	5
Ta	0.09	0.09	0.09	0.12	0.11	0.07	0.08	0.11	0.09	0.10	0.10	0.14	0.16	0.14	0.09		0.34	0.19	23	17
Tl	0.07	0.06	0.05	0.03	0.05	0.03	0.05	0.04	0.03	0.04	0.04	0.07	0.06	0.05	0.02		0.63	0.52	31	28
Pb	2.94	3.32	3.06	2.76	3.21	2.88	2.90	2.95	2.84	2.51	2.38	3.42	3.38	3.66	2.86		0.72	0.43	11	8
Th	0.65	0.77	0.61	0.49	0.56	0.55	0.59	0.59	0.48	0.48	0.44	0.80	0.78	0.79	0.71		0.94	0.87	19	16
U	0.42	0.49	0.41	0.33	0.40	0.40	0.40	0.38	0.34	0.32	0.31	0.49	0.46	0.49	0.39		0.86	0.70	15	12
La/Yb	3.14	3.55	3.36	2.92	3.50	3.01	3.30	3.39	3.01	2.69	2.74	3.93	3.79	3.73	4.03		0.75	0.71	12	12
Ba/Sr	1.01	1.01	0.90	0.76	0.82	0.95	0.90	0.82	0.84	0.77	0.79	1.09	1.06	1.07	0.92	0.93	0.90	0.89	12	12
U/Th	0.64	0.64	0.68	0.68	0.72	0.72	0.68	0.64	0.72	0.66	0.69	0.62	0.59	0.62	0.55		-0.74	-0.74	7	7
Cs/Rb	5.13	5.81	4.45	5.89	5.33	4.52	4.53	5.92	5.04	5.67	6.12	6.18	6.30	5.87	5.93		-0.80	-0.80	13	13

Tab. 3-3

Oxygen (in ‰ SMOW) and radiogenic isotope ratios for samples from Kluchevskoy volcano. Whole rock oxygen isotope ratios ($^{18}\text{O}_{\text{WR}}$) were calculated from the mean of olivine data, assuming an olivine-melt fractionation of -0.4 ‰. The outlier from KLU-10 (asterix) was excluded from this calculation.

Sample	Rock type	Phenocrysts	$^{18}\text{O}_{\text{ol}}$	$^{18}\text{O}_{\text{cpx}}$	$^{18}\text{O}_{\text{WR}}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{143}\text{Nd}/^{144}\text{Nd}$	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
KLU-01	HMB	plag, cpx, ol	6.90	6.51	7.27	0.70356	0.51309	18.31	15.50	37.97
			6.90	7.40						
			6.82	7.43						
KLU-03	HMB	ol, cpx	6.40	6.68	6.80	0.70357	0.51310	18.28	15.50	37.97
			6.36	6.45						
			6.32							
			6.50							
KLU-04	HMB	plag, cpx, ol	5.97	6.21	6.32	0.70353	0.51307	18.28	15.50	37.97
			5.86	6.43						
KLU-05	HMB	plag, cpx, ol	5.93		6.29					
			5.84							
KLU-06	HMB	ol, cpx	6.36	6.80	6.80	0.70355	0.51309			
			6.43	6.44						
KLU-07	HMB	ol, cpx	6.28	7.15	6.64	0.70355	0.51307	18.30	15.50	37.97
			6.19	7.07						
				6.77						
KLU-08	HMB	plag, cpx, ol	6.00	5.73	6.41	0.70352	0.51308	18.30	15.52	38.01
			6.01	6.49						
KLU-09	HMB	plag, cpx, ol	5.82	6.40	6.23	0.70351	0.51311			
			5.83	6.43						
				6.27						
KLU-10	HMB	plag, cpx, ol	5.85	6.57	6.22	0.70352	0.51311	18.29	15.51	38.00
			5.78	6.46						
			5.31*							
KLU-11	HMB	plag, ol, cpx	5.84	6.28	6.23	0.70353	0.51310	18.29	15.50	37.97
			5.82	6.56						
KLU-15	HMB	ol, cpx	6.95	7.26	7.34	0.70355	0.51312	18.30	15.49	37.94
			6.97	6.72						
			6.89							
KLU-16	HMB	ol, cpx	5.97		6.43					
			6.09							
KLU-02	HAB	plag (ol, cpx)	7.07	7.15	7.43					
			6.99	7.36						
KLU-12	HAB	plag (ol, cpx)	6.89	7.66	7.29	0.70366	0.51309	18.30	15.51	38.00
				7.22						
				7.21						
KLU-13	HAB	plag (ol, cpx)	7.13		7.53	0.70366	0.51309			
KLU-14	HAB	plag (ol, cpx)	7.05	7.63	7.47	0.70362	0.51309			
			7.09	7.56						
				7.73						

Tab. 3-4

Composition of components used in the mixing and AFC modelling.

	DM ¹	EM ²	IAB ³	sediment ⁴	slab fluid ⁵	arc crust ⁶
¹⁸ O _{WR} [‰]	5.7	5.8	5.7	20	12	8; 10; 12
O [%]	50	50	50	50	85	50
⁸⁷ Sr/ ⁸⁶ Sr	0.7028	0.7033	0.7033	0.707	0.7036	0.7046
Sr [ppm]	16.6	19	200	250	550	200

¹) Depleted mantle (DM): ¹⁸O and ⁸⁷Sr/⁸⁶Sr after Ito et al. (1987), Sr after McCulloch & Benett (1994)

²) Enriched mantle (EM) calculated as 99% DM + 1% sediment

³) Island arc basalt (IAB) assumed to be close in composition to these Kluchevskoy magmas with low δ¹⁸O

⁴) Sediment composition assuming to be in equilibrium with Cretaceous sea water, Sr after Bailey (1996)

⁵) Slab fluid derived from altered oceanic crust (Staudigel et al. (1996), Brenan et al. (1995))

⁶) The ¹⁸O value for arc crust correspond to AOC, ⁸⁷Sr/⁸⁶Sr and Sr were empirically derived to approximate the observed trends

Tab. 3-5

Rock and fluid compositions used in our model of mantle hydration (all concentrations in ppm). Differences between the compositions of the calculated fluids to these from the literature data (Brenan et al. 1995, Ayers et al. 1997) are caused by slightly different input parameter in the our modeling.

	EM ¹	Slab ²	Slab fluid (SF) ³		Wedge fluid (WF) ⁴		SF/WF	SF/EM
			A	B	A	B		
Rb	0.38	9.58	71		1.09		65	186
Ba	10.47	22.6		2210		173	13	211
Th	0.036	0.7		1.69		0.33	5.1	47
U	0.017	0.3		0.59		0.33	1.8	36
Pb	0.090	0.3		15		4.80	3.1	168
Sr	17.8	115	180	575	47	100	4-6	32
Nb	0.36	1.22	0.04	0.36	0.23	2.55	0.1-0.2	0.1-1.0
Zr	8.62	66.5	1.70		22		0.1	0.2
La	0.41	1.84	0.84		0.81		1.0	2.1
Sm	0.40	2.5	0.01		0.04		0.3	0.03
Tm	0.30	0.43	0.001		0.005		0.3	0.005
Y	22.6	26.9	0.03		0.41		0.1	0.001
U/Th	0.46	0.43		0.35		0.99	0.4	0.8
La/Tm	1.36	4.28	612		170		3.6	450
Ba/Sr	0.59	0.20		3.85		1.73	2.2	6.6

¹⁾ Enriched mantle calculated from depleted mantle (after McCulloch & Benett (1994)) contaminated by 0.5% sediment (after Bailey (1996))

²⁾ Slab composition after Staudigel et al. (1996), Pb after McCulloch & Gamble (1991)

³⁾ Calculated fluid (1%) in equilibrium with the slab (59:40:1 by mass garnet:clinopyroxene:rutile), using D_{mineral}/fluid values of Ayers et al. (1997) = A and Brenan et al. (1995) = B

⁴⁾ Calculated fluid (1%) composition in equilibrium with the EM (60:30:10 by mass olivine:orthopyroxene:amphibole), using D_{mineral}/fluid values of Ayers et al. (1997) = A and Brenan et al. 1995 = B

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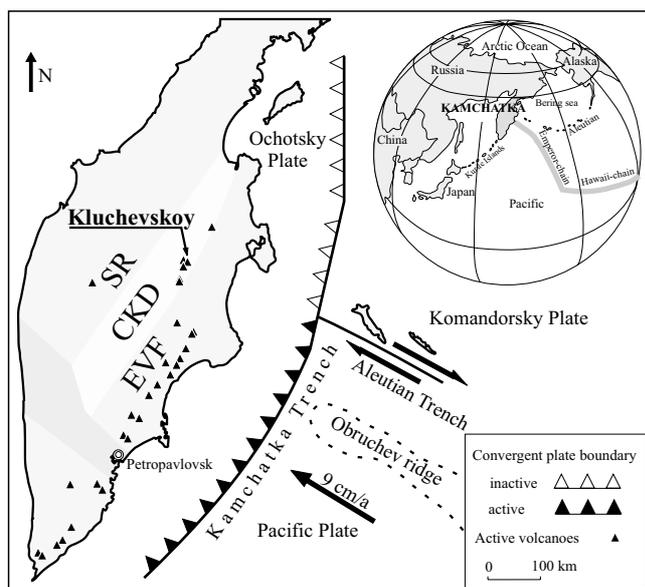


Fig. 3-1A
Kamchatka Peninsula: tectonic structure and active volcanism in the Eastern Volcanic Front (EVF), Central Kamchatka Depression (CKD) and Sredinny Ridge (SR). Modified after Erlich and Gorshkov (1979) and Fedotov and Masurenkov (1991).

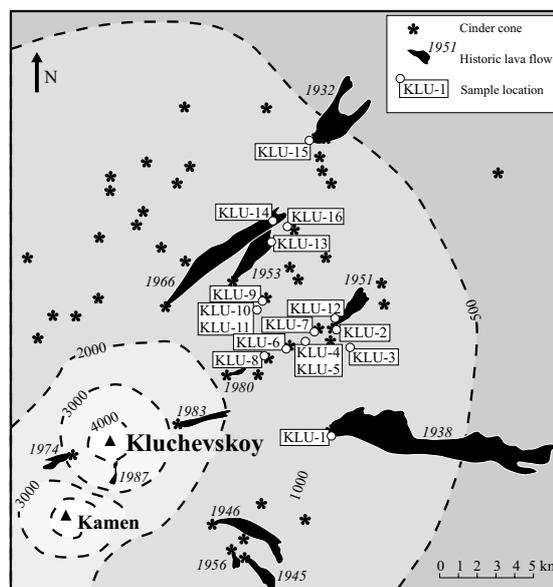


Fig. 3-1B
Cinder cones, historic eruptions and sample locations at Kluchevskoy volcano. Map after Khrenov et al. (1991).

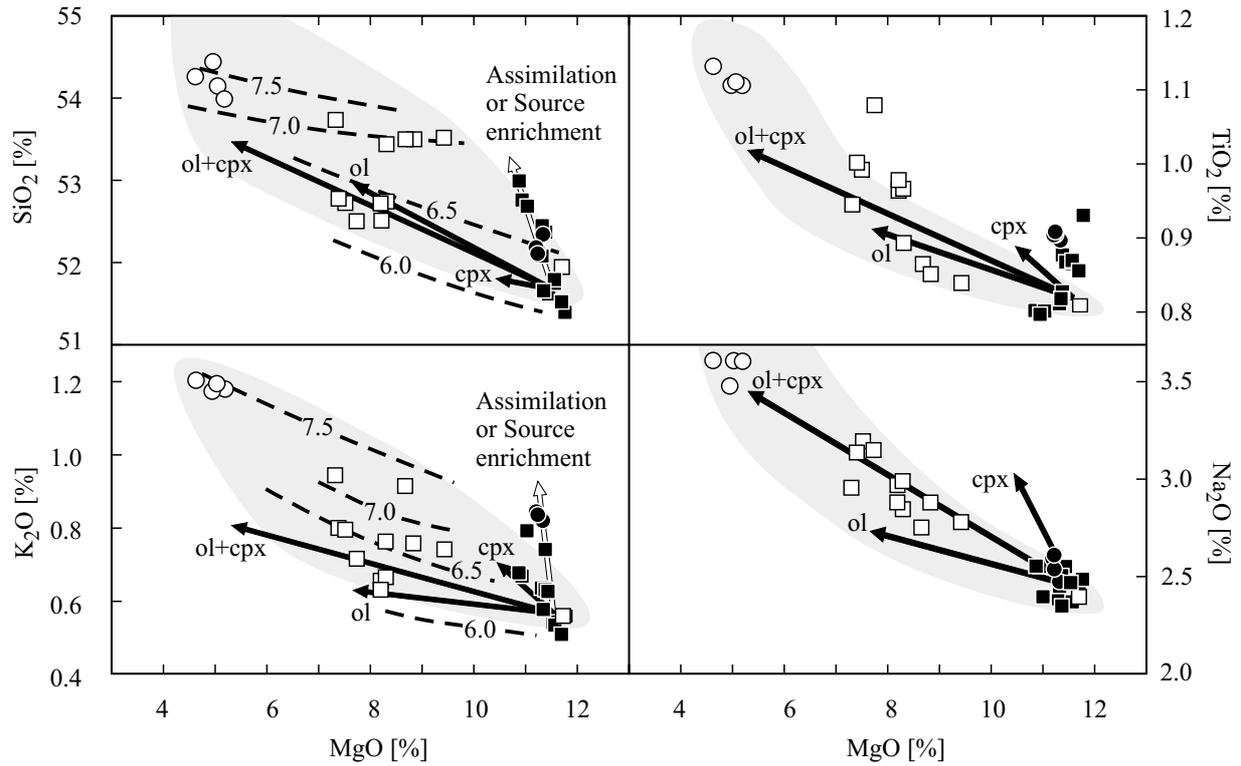


Fig. 3-2

Plots of MgO versus SiO₂, TiO₂, K₂O and Na₂O for Kluchevskoy samples. HAB and HMB are distinguished by open circles and squares, respectively. Closed symbols are calculated fractionation corrected primitive compositions for Mg#70 (see text for details). Vectors for 10 % olivine- (ol), 20 % clinopyroxene (cpx) and 10 % olivine + 20 % clinopyroxene (ol+cpx) fractionation are shown in each diagram. It is obviously from MgO versus K₂O and SiO₂ that beside fractional crystallization additional processes are necessary to explain the whole data range. Dashed lines in the plots of MgO versus SiO₂ and K₂O represent contours of δ¹⁸O (‰). The gray field represents the data for Kluchevskoy of Kersting and Arculus (1994).

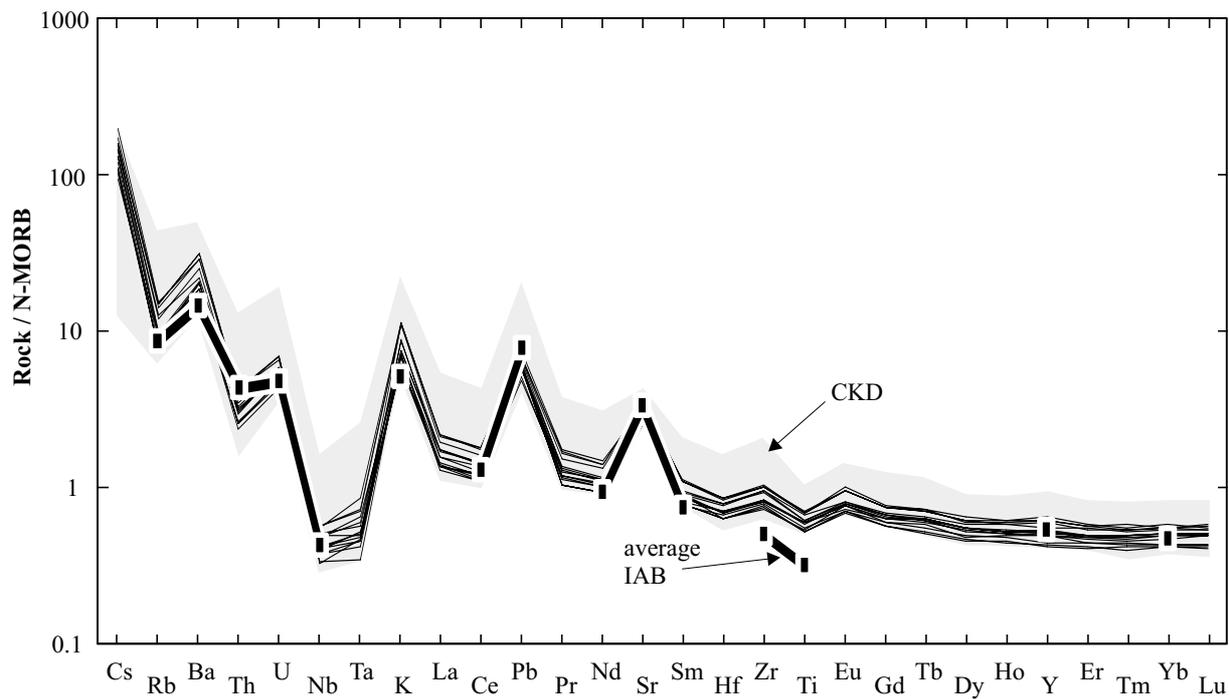


Fig. 3-3

N-MORB normalized trace element pattern of Kluchevskoy volcano/Kamchatka (thin lines). Note the typical arc signature with strong enrichment in LILE and depletion in HFSE, which do not differ from the whole field for rocks of the Central Kamchatka Depression (Churikova et al., 2000) or an average arc basalt (McCulloch and Gamble, 1991). N-MORB composition and the order of incompatible elements (enlarged by Cs and all REE) after Hofmann (1988).

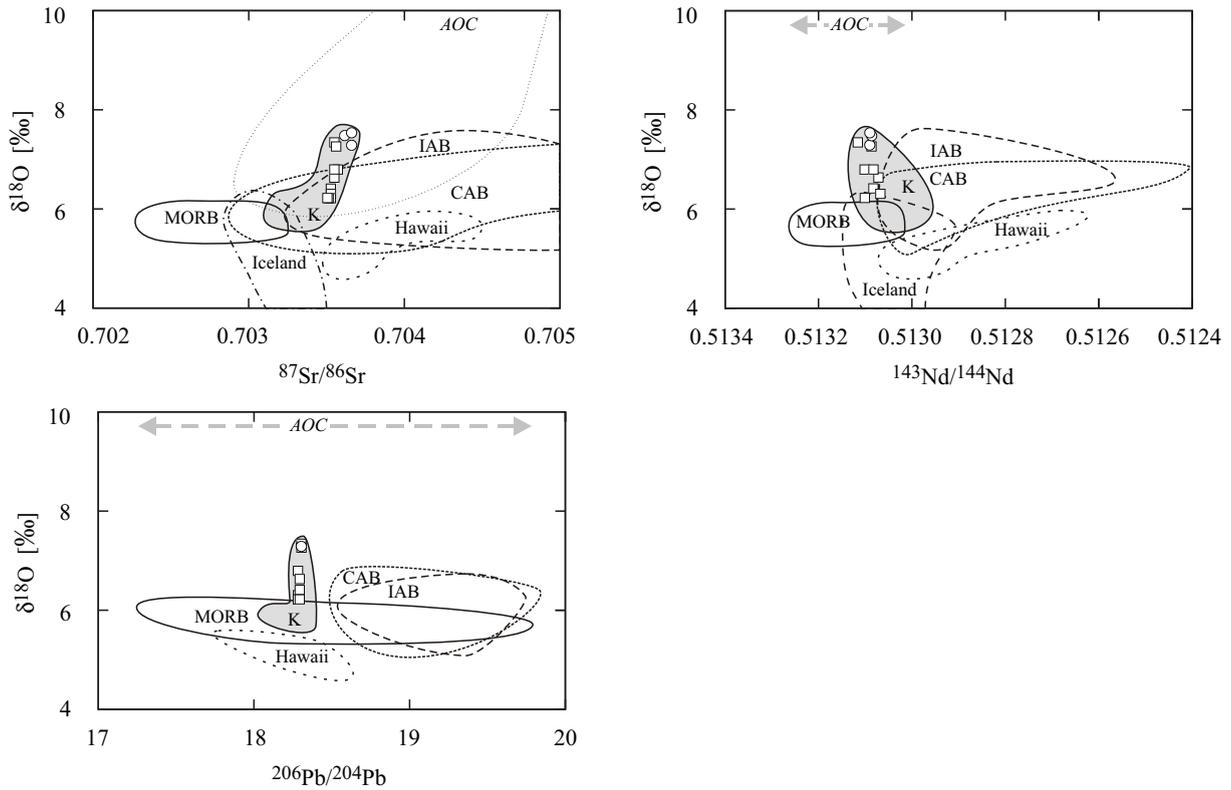


Fig. 3-4

Plots of Sr, Nd and Pb isotopic ratios versus $\delta^{18}\text{O}$. Symbols for Kluchevskoy samples correspond to Fig. 3-2. Fields for MORB, Iceland, CAB (continental arc basalts) and IAB (island arc basalts) are derived from a compilation for fresh basalts of Harmon and Hoefs (1995). The Hawaii data was taken from Eiler et al. (1996). The Kamchatka field (K) includes unpublished isotope data of the authors for the Eastern Volcanic Front, Central Kamchatka depression and Sredinny ridge. The altered oceanic crust is assumed to be similar in $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ to the MORB field, for $\delta^{18}\text{O}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ we used the bulk composition of AOC from Staudigel et al. (1996). From all oxygen data only the $\delta^{18}\text{O}$ values of Hawaii and Kamchatka were determined by laser ablation.

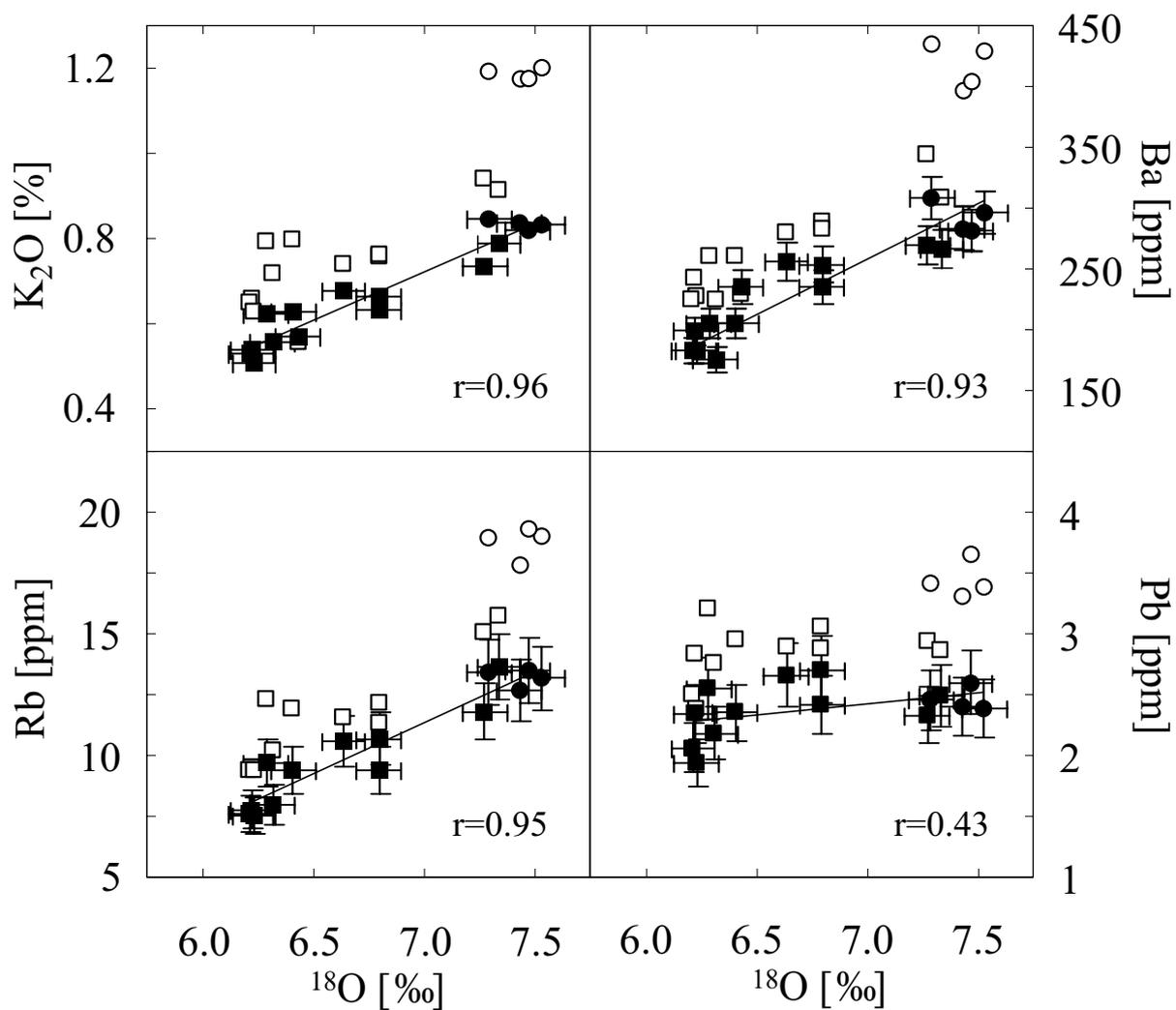


Fig. 3-5

Correlations of $\delta^{18}\text{O}$ with fluid mobile elements like K₂O, Ba, Rb and Pb. Same symbols like in Fig. 3-2. The analytical error, regression lines and regression coefficients are shown for the fractionation corrected data. Remarkable are the strong positive correlations for K, Ba and Rb but the weak positive trend for Pb.

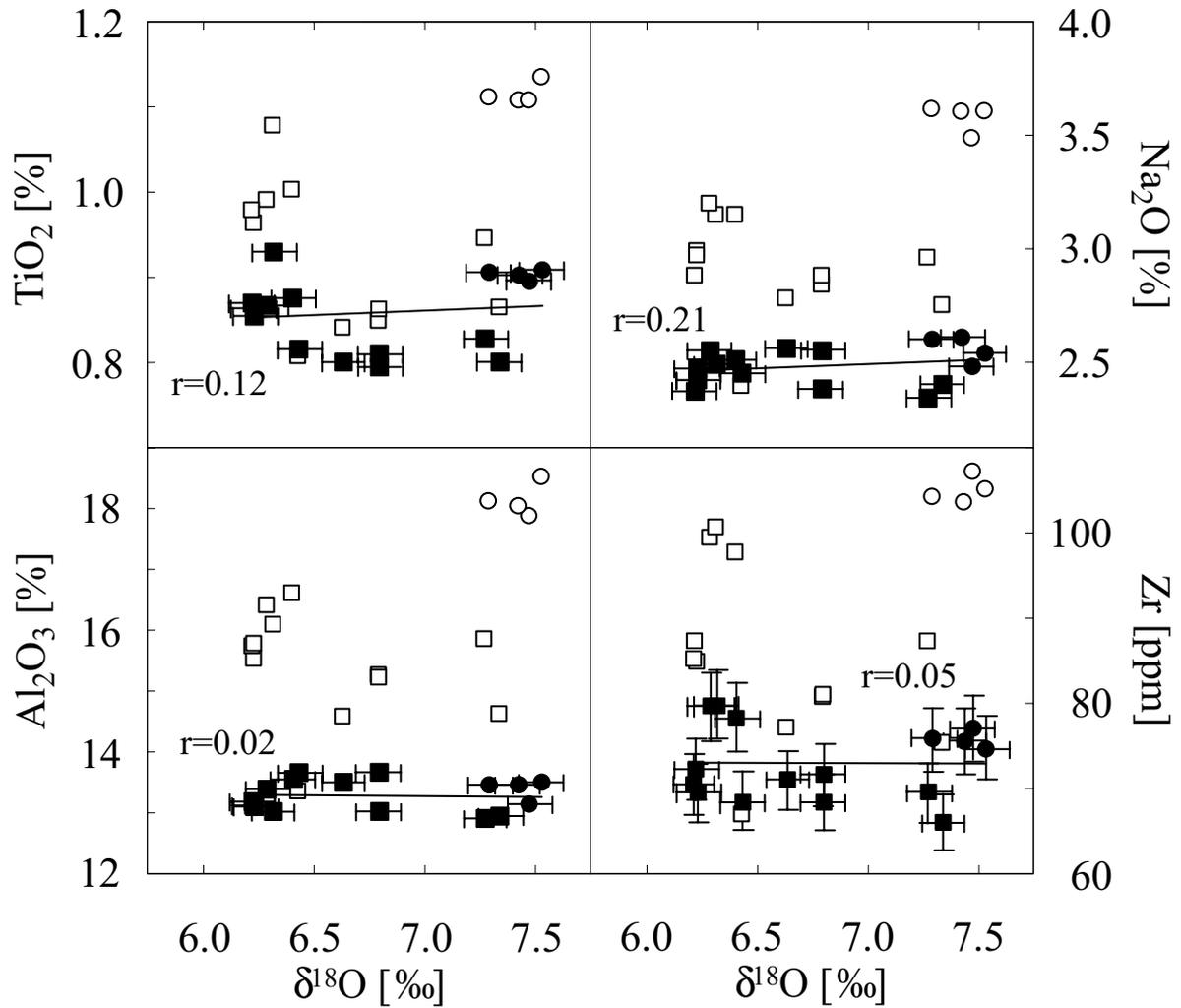


Fig. 3-6

Plots of $\delta^{18}\text{O}$ versus fluid-immobile but melt mobile elements like TiO_2 , Na_2O , Al_2O_3 and Zr . Same symbols like in Fig. 3-2. The analytical error, regression lines and regression coefficients are shown for the fractionation corrected data. Significant correlations cannot be observed for all elements of this group.

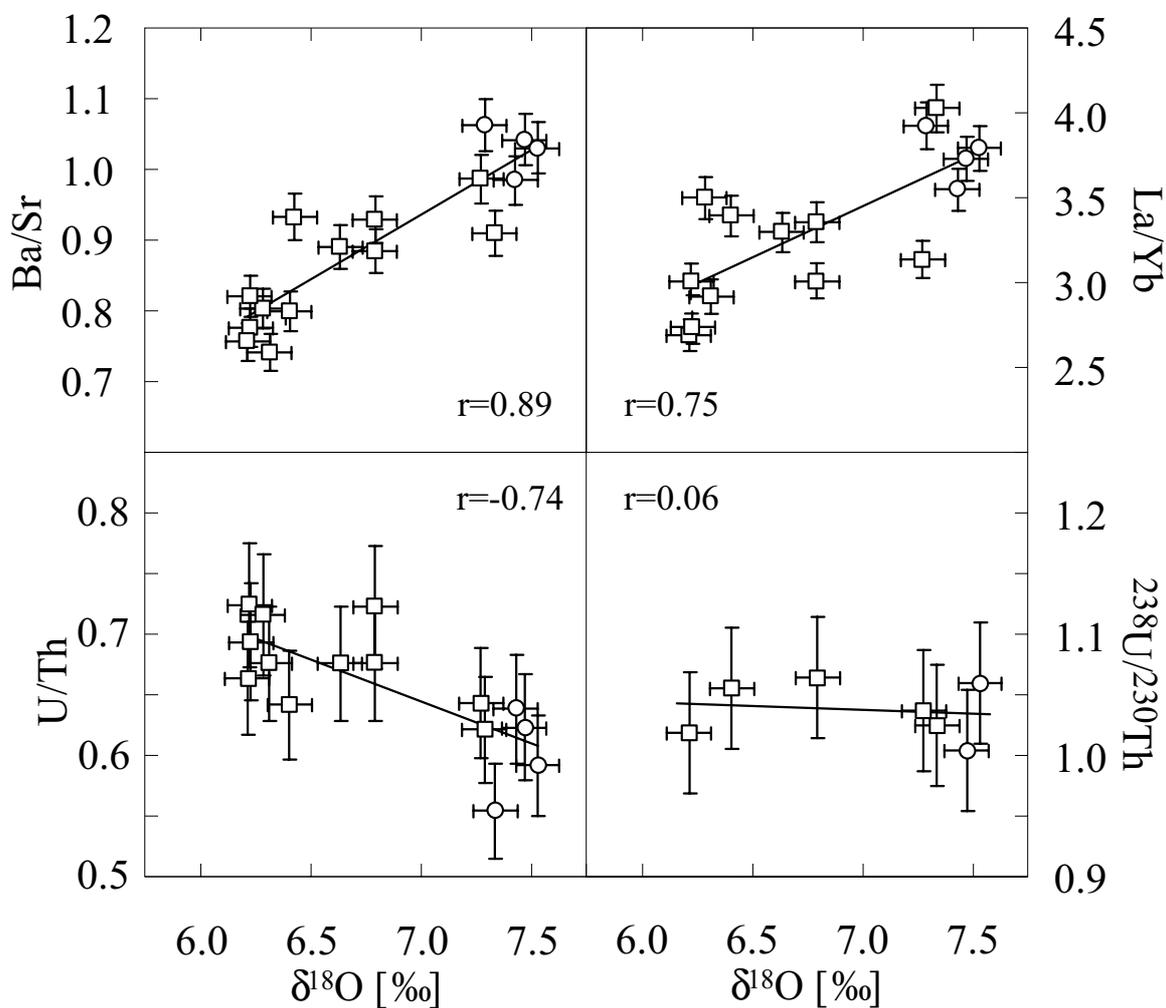
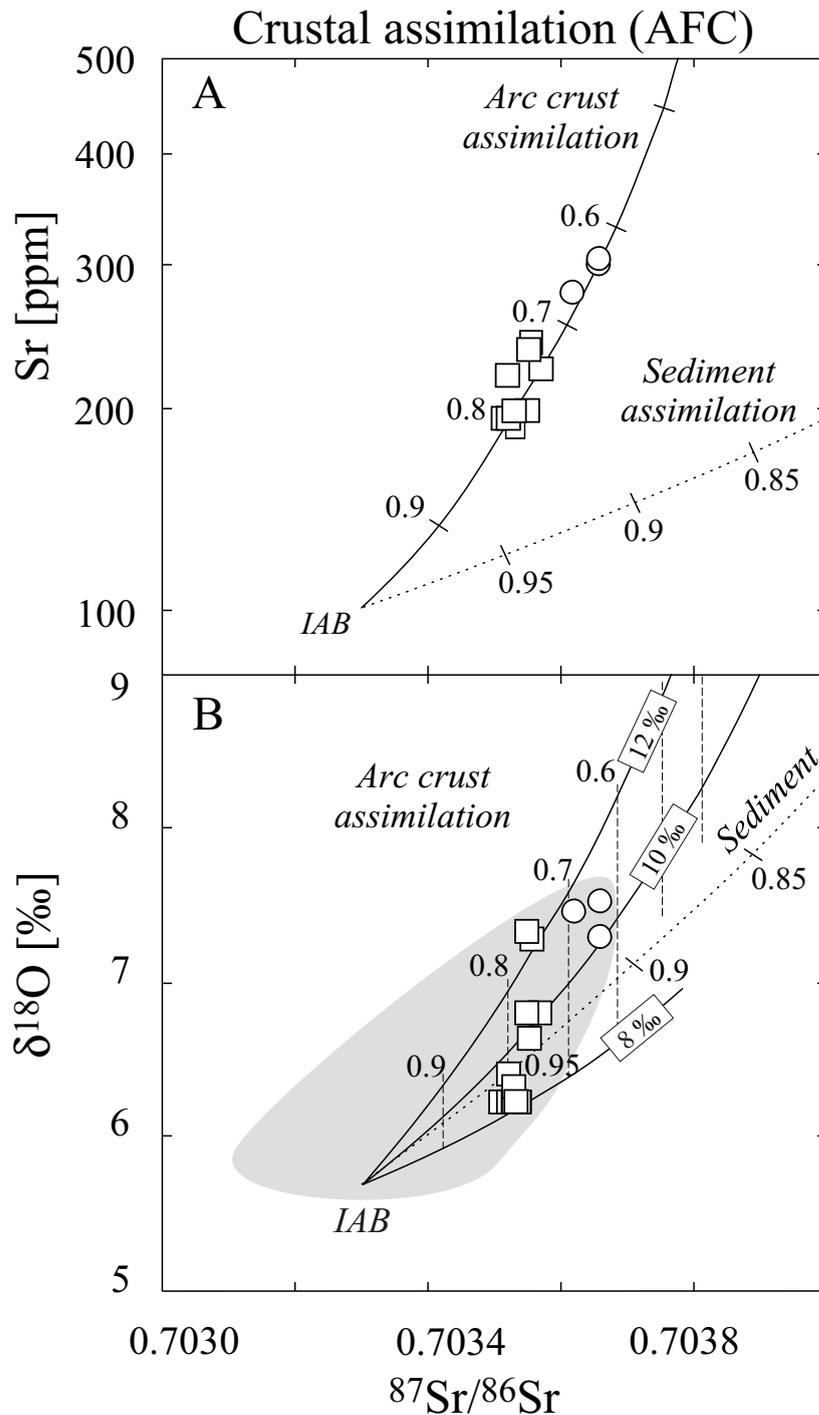
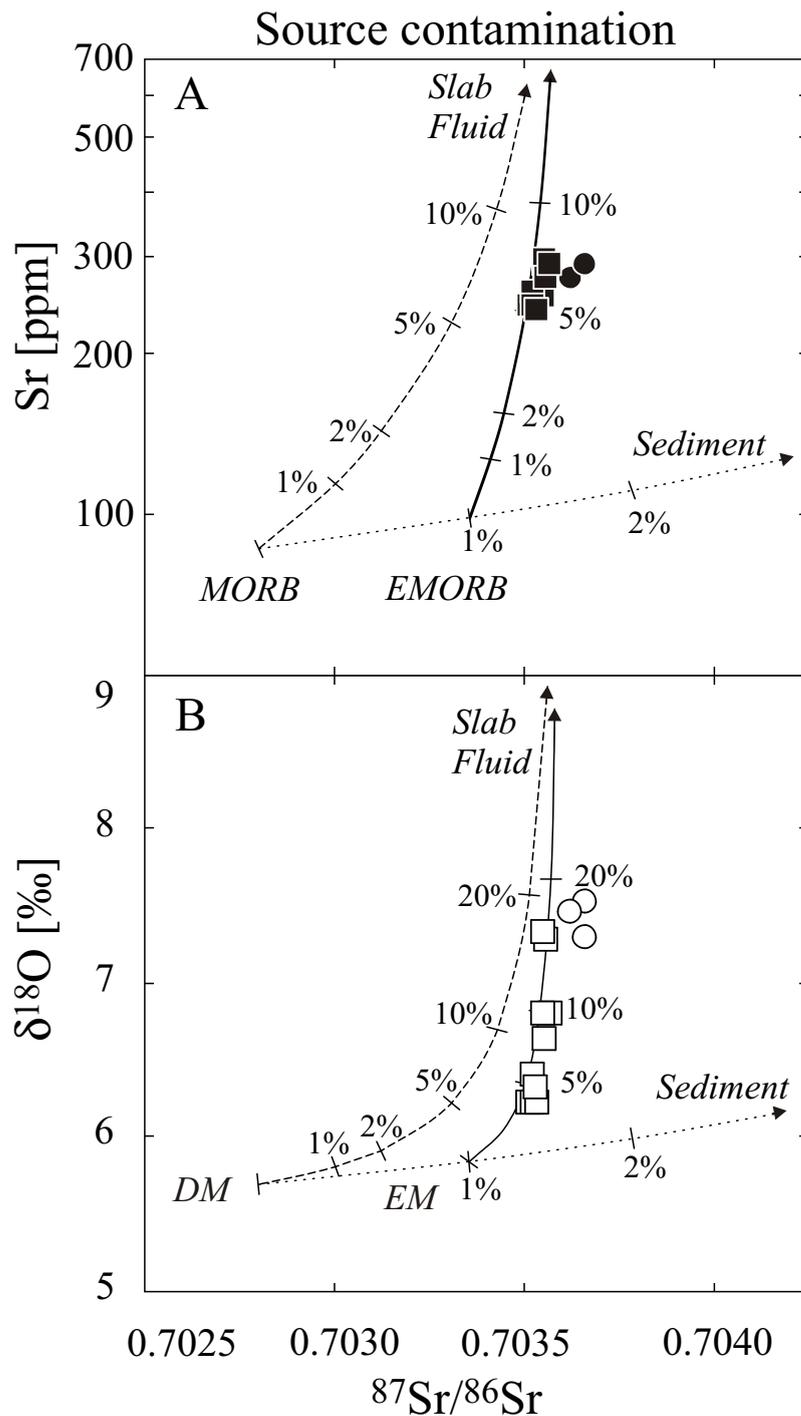


Fig. 3-7

Correlations of $\delta^{18}\text{O}$ with trace element ratios and the U-Th disequilibrium. It is assumed, that the shown trace element ratios are not significantly changed by olivine and clinopyroxene fractionation and partial melting. The analytical error (2σ), regression lines and regression coefficients are shown additionally. Despite a negative correlation of $\delta^{18}\text{O}$ versus U/Th no correlation with the U-Th disequilibrium exist.

**Fig. 3-8**

AFC model, calculated for assimilation of hydrated ^{18}O -enriched island arc crust or sediment by primitive island arc basalts (IAB). The data trends can be best explained by assimilation of island arc crust with variable $\delta^{18}\text{O}$ but a similar Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ composition. The ratio between assimilation and fractional crystallization is set to 0.5. Tick marks express F, the remaining melt fraction. Compositions of the used components in the modeling are shown in Tab. 3-4. Symbols like in Fig. 3-2, the gray field represents the data for basalts from all Kamchatka (unpublished data of the authors).

**Fig. 3-9**

Mixing model between depleted mantle (DM) or enriched mantle (EM) and slab fluid, derived from the altered oceanic crust and between DM and sediment. Lines in Fig. 3-8A represent melts, derived from 10% melting of such contaminated mantle, the degree of source contamination is shown by tick marks. Mg#70-normalized data was used to compare it with the Sr concentrations in the magmas, derived from the modeled variably enriched sources. The gray field represents the data for basalts from all Kamchatka (unpublished data of the authors). Sample symbols like in Fig. 3-2. Mixing end members are derived from Tab. 3-4.

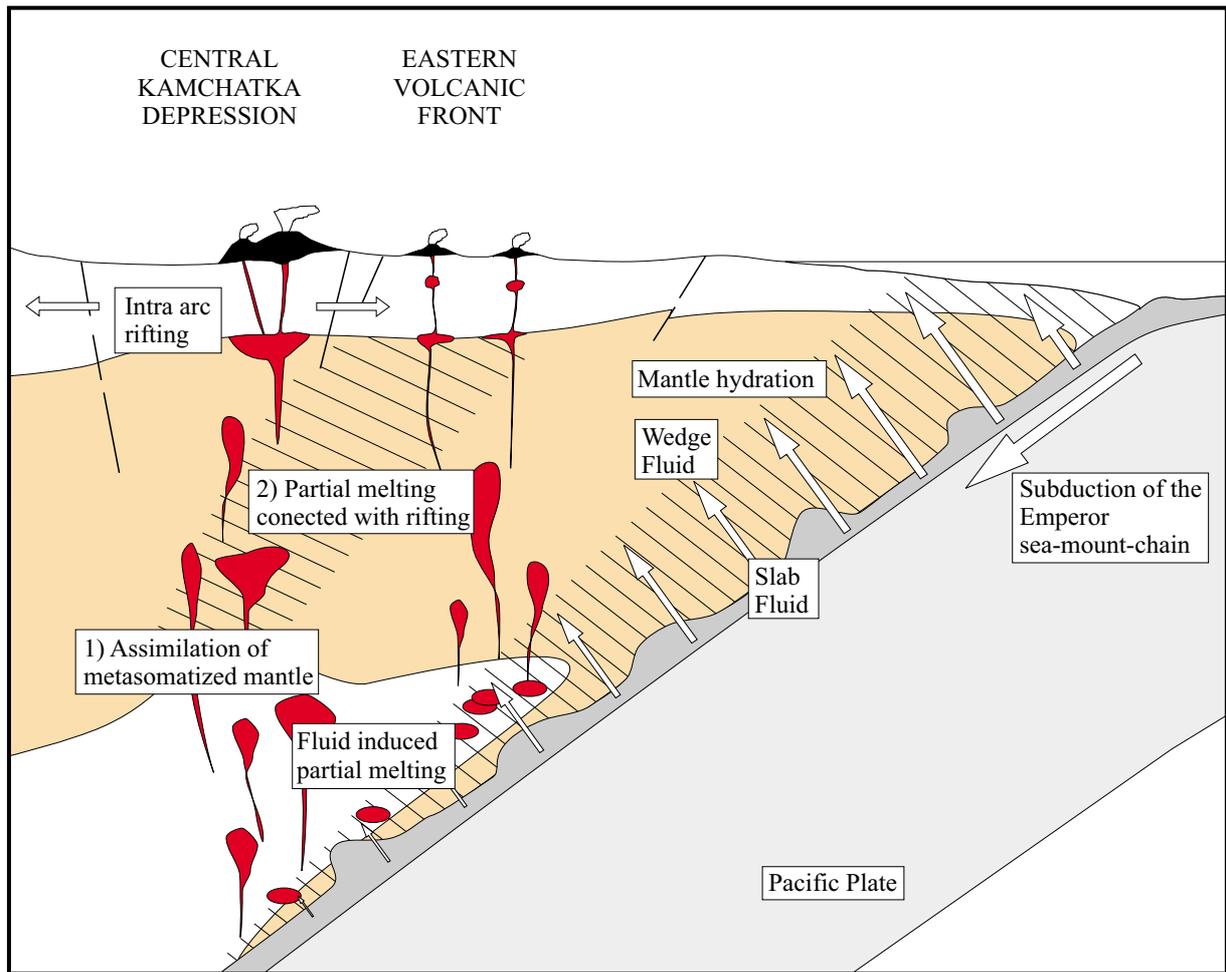


Fig. 3-10

Model of sub-arc lithospheric metasomatism, which can explain the strong ^{18}O - and fluid-mobile element enrichment in primitive basaltic andesites of Kluchevskoy volcano. Special features of the subducting slab (old low-T altered ocean island chain, fast subduction) led to an influx of large amounts of fluid into the mantle. The lithospheric part of the mantle is too cold to melt but gets enriched in fluid-mobile elements and ^{18}O . Accretional tectonic transport such as metasomatized mantle below the Central Kamchatka Depression, where it can be presently involved in arc magmatism by 1) assimilation of enriched lithospheric mantle by melts from the asthenospheric mantle or 2) partial melting of the enriched lithospheric mantle, caused by the recent intra-arc rifting