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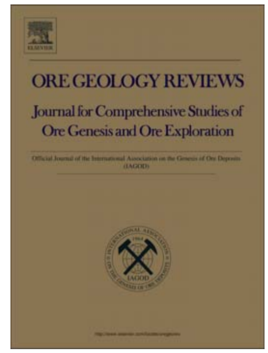

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Lead isotopic systematics of massive sulphide deposits in the Urals: applications for geodynamic setting and metal sources

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Abstract

Lead isotopic compositions of 61 samples (55 galena, one cerussite [$PbCO_3$] and five whole ore samples) from 16 Volcanic Hosted Massive Sulphide (VHMS) deposits in the Urals Orogeny show an isotopic range between 17.437 and 18.111 for $^{206}Pb/^{204}Pb$; 15.484 and 15.630 for $^{207}Pb/^{204}Pb$ and 37.201 and 38.027 for $^{208}Pb/^{204}Pb$. Lead isotopic data from VHMS deposits display a systematic increase in ratios across the Urals paleo-island arc zone, with the fore-arc having the least radiogenic lead compositions and the back-arc having the most radiogenic lead. The back arc lead model ages according to Stacey-Kramers model are close to the biostratigraphic ages of the ore-hosting volcano-sedimentary rocks (*ca*. 400 Ma). In contrast, less radiogenic lead from the fore-arc gives Neoproterozoic (~700 Ma) to Cambrian (480 Ma) lead model ages with low two-stage model μ values of 8.8 (parameter $\mu = ^{238}U/^{204}Pb$ reflects the averaged U/Pb ratio in the lead source), progressively increasing stratigraphically upwards to 9.4 in the cross-section of the ore-hosting Baymak-Buribai Formation. The range of age-corrected uranogenic lead isotopic ratios of the volcanic and sedimentary host rocks is also quite large: $^{206}Pb/^{204}Pb$ =17.25-17.96; $^{207}Pb/^{204}Pb$ = 15.48-15.56, and generally matches the ores, with the exception of felsic volcanics and plagiogranite from the Karamalytash Formation being less radiogenic compare to the basaltic part of the cross-section, which would potentially imply a different source for the generation of felsic volcanics. This may be represented by older Neoproterozoic oceanic crust, as indicated by multiple Neoproterozoic ages of mafic-ultramafic massifs across the Urals. The relics of these massifs have been attributed by some workers to belong to the earlier Neoproterozoic stage of pre-Uralian ocean development. Alternative sources of lead may be Archean continental crust fragments/sediments sourced from the adjacent East-European continent, or Proterozoic sediments accumulated near the adjacent continent and presently outcropping near the western edge of Urals (Bashkirian anticlinorium). The contribution of Archean rocks/sediments to the Urals volcanic rock formation is estimated to be less than 0.1% based on Pb-Nd mixing models.

The most radiogenic lead found in VHMS deposits and volcanics in the Main Uralian Fault suture zone, rifted-arc and back-arc settings, show similar isotopic compositions to those of the local Ordovician MORBs, derived from highly depleted mantle metasomatized during dehydrational partial melting of subducted slab and oceanic sediments. The metasomatism is expressed as high Δ $^{207}Pb/^{204}Pb$ values relative to the average for depleted mantle in the Northern hemisphere, and occurred during the subduction of oceanic crust and sediments under the depleted mantle wedge. A seemingly much younger episode of lead deposition with Permian lead model ages (*ca*. 260-280 Ma) was recorded in the hanging wall of two massive sulphide deposits.

Keywords: Pb isotopes; Urals, island arc; massive sulphide deposits

1. Introduction

Island arc systems are considered the major sites of crust-mantle interaction where the lithospheric materials including altered oceanic crust and sediments are returned to the deep mantle as continental lithosphere is being produced. Island arc magmatism generated above a subducted oceanic plate is derived both from the slab and from the overlying mantle wedge. High-pressure dehydration of subducted crust releases fluids that act as a flux for the melting of mantle wedge peridotites and generation of arc magmas (e.g., Hofmann 1997). During dehydration of the slab, crustal lead migrates into the overlying mantle wedge leading to an enrichment in lead in arc magmas and ultimately to high lead concentrations in the continental crust and consequently in VHMS deposits (Plank and Langmuir 1998). The lead isotopic composition of massive sulphides and host rocks of recent and ancient VHMS deposits, associated with the mid-ocean ridges and island arcs, have been studied by a number of workers (e.g. Fouquet and Marcoux 1995; Ellam et al. 1990). The isotopic composition of lead from deposits and host rocks of the Mid-Atlantic ridge is remarkably homogeneous and corresponds to the host MORB (Mid-Ocean Ridge Basalts). In contrast, the isotopic composition of lead in massive sulphides and rocks from island arcs varies more widely as is the case for the Mesozoic Japanese island arc (Tatsumoto, 1969) and the Tertiary Macuchi island arc (Chiaradia and Fontboté, 2001). This has been explained in terms of a variable contribution of lead from the subducted oceanic crust and sediments into the ore-forming fluids. Another potential source of lead in intra-oceanic island arc constitutes the cryptic relics of continental crust which can be rifted and dragged far from original continent within the basement of arcs, as it is the case in modern intra-oceanic arc Vanuatu (Buys et al., 2014) and the Solomon island arc (Tapster et al., 2014).

Thus, the significant differences among lead isotopic ratios within volcanic rocks in subduction zones is usually interpreted as a mixture of material derived from the subducted slab and the mantle wedge. The subducted slab consists of oceanic crust (characterized by a μ [$^{238}U/^{204}Pb$] ~8) and pelagic or continental sediments with a radiogenic component expressed in high $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios. The sediment contribution can sometimes dominate the lead isotopic budget for some arcs (e.g., the Luzon arc, McDermott et al. 1993). The fluid/melt derived from the slab for continental arcs can be masked by the assimilation of arc crust (Hildreth and Moorbath 1988). Intra-oceanic arcs are therefore more appropriate sites for distinguishing the isotopic composition of slab-derived fluid, e.g. the Izu-Bonin arc (Taylor and Nesbitt 1998). Studies of the Mariana subduction zone have shown that lead is lost at a shallower depth, and U at a deeper depth from subducted altered oceanic crust, with about 44-

75% of lead and <10% of U lost from altered oceanic crust to the arc, and a further 10-23% of lead and 19-40% of U lost to the back-arc (Kelley et al. 2005). The lead isotopic composition of back-arc material could be representative of the mantle wedge with a minor input of the slab component. Thus, the main question in interpreting of island-arc system formation has been to distinguish the signatures derived from the slab (and subducted sediments) and those derived from the overlying mantle wedge.

In general, the lead isotopic data found within an island arc setting cannot be explained by a simple mixing line between depleted MORB or OIB and the continental crust (Hofmann 1997). Notably, U/Pb and Th/U ratios can be affected by magma generation and fractionation, by hydrothermal and metamorphic processes or by weathering (release of U). For example, the inverse correlation of $^{238}U/^{204}Pb$ and $^{206}Pb/^{204}Pb$ ratios across the Japanese island arc has been explained by preferential extraction of lead relative to uranium at shallow depths (Tatsumoto 1969).

The Urals offers the chance to study a complete cross-section across the well-preserved Palaeozoic island-arc system from a boninite-like and calc-alkaline fore-arc sequence of the Baymak-Buribai series to the mainly tholeiitic island-arc Karamalitash Formation in an arc setting, and tholeiitic to calc-alkaline rocks of the Kiembay Formation in the back-arc setting. A number of massive sulphide deposits occur within the fore-arc, arc and back-arc geotectonic settings. The first investigation of lead isotopic composition in VHMS deposits of the Urals was made by Vinogradov et al. (1960) who concluded that the majority of the Urals VHMS deposits were formed in Carboniferous time and the lead isotopic compositions of the Urals deposits is very close to that of the VHMS deposits hosted by rocks of the same age in the Priirtishskaya zone of the Altay. The oldest Lower Palaeozoic deposits Ivanovskoye and Uluk are hosted by an ophiolite sequence within the Main Urals Fault Suture Zone and have a mantle affinity. Ershov and Prokin (1992) proposed that old crustal lead with a model age of 1,900 Ma had contributed to the Formation of massive sulphide systems in the Urals, suggesting that blocks of old crustal rocks could exist at depth in the mantle. The same conclusion concerning the contribution of old crustal lead to VHMS deposits formation was reached by Sundblad et al. (1996) who studied lead isotopic compositions in some Urals-type (Uchaly, Molodezhnoye, Safyanovskoye deposits) and the Bakr-Tau deposit of Baymak type which show an average $^{206}Pb/^{204}Pb$ ~17.7 and μ ~9.6-9.7. These authors proposed crustal contamination by Riphean platform sediments, similar to the rocks of the Bashkirskiy anticlinorium, which would have contributed to the source of the volcanic rocks in Magnitogorsk zone. Brown and Spadea (1999) further developed this idea of a continental contribution, which is supposed to be a part of the East European craton, referring in particular to the Maksutovo Complex that has been dragged into the subduction zone. For this reason, the tectonic development of the Urals can be compared to that of the Papua New Guinea, Timor and Taiwan volcanic arcs where volcanism stopped shortly after the entry of continental crust into the subduction zone.

The most recent paper describing the lead isotopic composition of massive sulphide deposits in Urals was published by Chernyshev et al. (2008) who studied galenas from 13 massive sulphide deposits situated in the Middle and Southern Urals. They concluded that the ancient continental crust of the eastern island-arc margin and marine sediments of the Devonian volcano-sedimentary sequences played a crucial role in the contamination of primary mantle melts with crustal material. The trend of increasing second stage μ(2) values in the ore-hosted lead from Silurian and Early Devonian (9.48–9.54) to the Middle Devonian (9.66–9.83) was attributed to an increase in the differentiation degree of magmas and the maturity of the crust.

In this paper, the application of lead isotopic compositions as a means of testing the role of subducted oceanic lithosphere versus continental crust in the source of lead in 16 VHMS deposits of the Urals arc is investigated.

2. Tectonic setting

2.1 Urals

The Urals is a well-mineralised orogenic belt, approximately 2000 km long, and was formed during Late Devonian – Early Carboniferous time as a result of the collision between the proto-Uralian island arc and the East European (also called Laurussia) and Kazakhstan continents (Borodaevskaia et al. 1977; Zonenshain, 1984; Puchkov, 1997; Koroteev et al. 1997; Brown et al. 2001; Seravkin et al.

1994, Zaykov et al. 1996, Herrington et al. 2005). The structure of the Urals, and in particular that of the Southern Urals, is well-preserved. The following subdivisions can be made (Fig. 1):

(1) Main Uralian Fault (MUF) suture zone with relics of ophiolite in a tectonic melange containing blocks with ages ranging from Ordovician up to Late Devonian.

(2) Magnitogorsk island arc zone, consisting of Devonian volcanic and sedimentary rocks. An intermediate "inter-arc" basin, filled by Late Devonian-Lower Carboniferous volcanic and sedimentary rocks, divides the Magnitogorsk structure into the West and East-Magnitogorsk zones;

(3) Sakmara allochthon, consisting of several tectonic sheets, composed of bathyal sediments of the continental margin (Puchkov, 2000), overlain by Ordovician (Ryazantsev (2010) and Devonian island arc complexes and ophiolites hosting VMS deposits.

The ages of the volcanic and sedimentary rocks in the Urals are mainly based on detailed biostratigraphic studies (Maslov and Artushkova, 2010) and range from Ordovician to Carboniferous (Puchkov, 1997). The formation of the massive sulphide deposits in the Urals began in Early Silurian times with the formation of the Yaman-Kasy deposit hosted by the Sakmara allochton. The deposits found in the Baymak-Buribai Formation were formed in the Emsian (407-398 Ma), whereas the majority of the deposits hosted by the Karamalytash Formation were formed in the Eifelian-Givetian (398-385 Ma).

2.3 Massive sulphide deposits

The isotopic compositions of lead from 16 VHMS deposits were analysed during the present investigation (Fig. 1). Overviews of the VHMS deposits in the Urals and their geotectonic settings are reported in Maslennikov and Zaykov (1998), Prokin and Buslaev (1999), Herrington et al. (2002). In the literature the Urals VHMS deposits are variably classified but we point the reader to a comparison of nomenclature published in Herrington et al. (2005). Here, we give only a short description of the studied VHMS deposits from west to east.

Main Uralian Fault (MUF) suture zone. The MUF suture zone occurs between the East European craton and the Magnitogorsk arc (Brown and Spadea, 1999). It is a mélange zone containing ophiolite fragments, volcanic rocks derived from the arc, and sediments from the fore-arc basin (Spadea et al. 2002). The MUF zone is the host for three Cyprus-type deposits: Ishkinino, Dergamish and Ivanovskoye (Melekestzeva et al. 2013). These deposits are hosted by mafic-ultramafic rocks within the fore-arc zone, and enriched in Ni and Co. The parental magma of the Ivanovskoye and Ishkinino deposits has a tholeiitic to boninitic affinity and probably formed in an early arc or fore-arc setting (Tesalina et al. 2003).

Magnitogorsk zone

West-Magnitogorsk zone. The Baymak district contains about 20 massive sulphide deposits and several non-industrial ore mineralization occurrences. The deposits are relatively small in size and are characterised by elevated Ag, Au and Zn contents. The deposits in this area are confined to tholeiitic and calc-alkaline rocks of the Baymak-Buribai Formation, which are characterised by LREE – enriched compositions (Herrington et al. 2002).

The *Oktiabrskoye* deposit occurs within the Makan ore field. The footwall of this structure consists of mafic volcanic rocks with a boninitic affinity in the lower section of the Baymak-Buribai Formation in a fore-arc setting (Herrington et al. 2002; Spadea et al. 1998). The *Bakr-Tau* deposit is mainly hosted by mafic volcanic rocks, which are cut by a sub-volcanic quartz porphyry intrusion. Half of this deposit consists of disseminated mineralization in feeder veinlets restricted to the sub-volcanic body. The veinlets are considered to be hydrothermal-metasomatic (Prokin and Buslaev 1999). The polymetallic *Uvariazh* deposit is hosted by felsic volcanic rocks and a streaky-disseminated style of mineralization is prevalent. The Gai deposit is one of the largest VHMS deposits in the Urals and is located in felsic and mafic volcanic rocks of the Baymak-Buribai Formation. The relatively small Au-Ag-Zn-rich polymetallic *Balta-Tau* deposit is located 10 km east of the Bakr-Tau deposit. The ore mineralization has the form of an extensive feeder zone and a relatively small sphalerite-dominated lens of massive ore. The ore body is located in a subvolcanic felsic porphyry intrusion in the upper part of the Baymak-Buribai Formation or lower part of Irendyk Formation (Holland, 2004). The host for the Podolskoe deposit is not clear, but it is probably in the upper parts of the Baymak-Buribai Formation (Herrington et al. 2005).

Inter-arc zone. The *Sibay* deposit is a major Urals type deposit and is hosted by tholeiitic volcano-sedimentary rocks of the Karamalytash Formation. This Formation is characterised by LREE depletion, typical of volcanic rocks developed in a rifted arc setting (Herrington et al. 2002). The Eu anomalies within the felsic rocks indicate a high degree of plagioclase fractionation.

East-Magnitogorsk zone. The giant Urals type VHMS deposits Uchaly and Molodezhnoe are hosted by the Karamalytash volcano-sedimentary Formation that forms part of the East-Magnitogorsk zone. The Alexandrinskoye deposit is the only example of a Baymak type deposit in the Karamalytash Formation. However, the presence of both tholeiitic and calc-alkaline volcanic rocks in the Alexandrinskoye district has been documented (Surin, 1993; Herrington et al., 2002). The high MgO boninite-like basalts in the Alexandrinskoye district show a similarity with boninite-like volcanic rocks from Shankai River and the upper Baymak-Buribai Formation and contrast with the Karamalytash rocks (Herrington et al., 2002), which makes its stratigraphic setting unclear.

Dombarovka back-arc zone. This ore region is located in the southern part of the East-Magnitogorsk zone and hosts two deposits studied in this work – Barsuchii Log and Dzhusa. The Kiembay Formation at the base of volcanic cross-section corresponds to the upper part of Baymak-Buribai and Irendyk Formations in the western zone. The basalts are close to MORB and continental tholeiites (traps). The primitive island arc volcanic rocks show calc-alkaline affinity (Puchkov 2000). Some authors consider that these volcanic rocks originated in a back-arc setting (Yazeva and Bochkarev, 1998).

Sakmara zone. The Mednogorsk ore district is located within the allochtonous Sakmara zone. The massive sulphide deposits in this terrain are hosted by an early Silurian volcano-sedimentary sequence (Herrington et al., 2002 and references therein). The studied Yaman-Kasy deposit is hosted by a bimodal sequence of tholeiitic to calc-alkaline rocks, which probably originated in an arc setting (Herrington et al., 2002).

2.4 Lead occurrences within Proterozoic and Ordovician sediments

As discussed above, the lead isotopic composition of the ore-forming fluids within an island arc setting has variable contributions from the subducted slab/sediments and possible continental blocks. These end-members may be best approximated using existing local lead occurrences within the Uralian Orogeny.

Bashkirian anticlinorium. The Bakal iron deposits are hosted by Neoproterozoic carbonate-rich sedimentary rocks within the Bashkirian anticlinorium in the Southern Urals (Herrington et al. 2005). These rocks represent a fragment of the epicratonic riftogenic-depressional sedimentary basins, which was developed near the margin of the East-European craton (Fig. 1) in Proterozoic times. This anticlinorium comprises terrigenous and carbonate deposits of the Bakal Formation (1,200-1,400m thick), hosting the Bakal iron deposit. This deposit consists of siderite and oxidized Fe ores (80-95 vol%), the rest (15-20 vol%) are dolomite, ankerite and barite. Galena and other sulphides are present as accessory minerals. The Pb-Pb model age of ore-hosting limestones from this deposit is 1,430±30 Ma (Kuznetsov et al., 2005). The Bakal deposit was included into this study in order to approximate the lead isotopic composition of the Proterozoic rocks/sediments.

Polar Urals. The Saureyskoe Cu-Zn barite-polymetallic stratiform deposit is hosted by a Mid-Upper Ordovician platform comprising a sequence of terrigeneous and carbonate rocks in the Polar Urals. It is used in order to estimate the lead isotopic composition of Ordovician sediments in the Urals.

3. Sampling

Most of the galenas were obtained from massive ores and from the footwall stockwork zones of the VHMS deposits studied in this work (Fig. 1). One cerussite [$PbCO_3$] sample was collected from continental weathering zone at the top of the Alexandrinskoye deposit. Two galena samples were collected from the hanging walls of VHMS deposits: one from the later quartz-barite vein cross-cutting the hanging wall sequence of the Alexandrinskoye deposit; and another one from a nodule within the hanging-wall sequence of the Uchaly deposit.

The ore deposits from the Main Urals suture zone (Dergamish, Ivanovka and ishkinino) mainly consist of pyrite and pyrrhotite, and do not contain any galena. From those deposits, representative samples of massive sulphide ores were collected.

In addition to sulphide ores, thirty two samples of volcanic and sedimentary rocks from the ore-hosting sequences, including volcanic and sedimentary rocks, have been selected for this study. The rocks samples were collected from the: (i) Main Uralian Fault suture zone; (ii) Bogachev plagiogranite massif from the Baymak-Buribai Formation; (iii) Irendyk Formation; (iv) Karamalytash Formation; (v) Mednogorsk ore region; as well as (vi) volcano-sedimentary rocks and plagiogranites within the Alexandrinskoye ore field.

4. Analytical methods

4.1 Lead isotope analyses

A detailed description of sulphide sample preparation and analytical methods is given in Pomiès et al. (1998). The galena was separated from the whole ore samples under a microscope, washed with deionised water and then dissolved in HBr. Dried supernate was then dissolved in 6N HNO_3 and directly loaded on a filament for mass-spectrometry. The massive sulphide (mainly pyrite) samples were also dissolved in HBr in order to eliminate microscopic galena. The sulphide was rinsed with dilute HCl and deionised water and dissolved for 12 hours in HCl 6N, HNO_3 6N and 1 drop of HBr in Teflon beakers. After drying down, this step was repeated. Lead was separated from the supernatant fluid using an HBr-HCl anion exchange method.

The whole rocks powders were dissolved in HF+HNO_3 over 72 hours on a hot plate. The dried residues were dissolved in 6N HCl, then heated again and evaporated. The residue was dissolved in HNO_3 6N and lead was separated with an ion exchange AG1X8 column.

Lead isotopic analyses were performed at BRGM (Orléans) using a Finnigan MAT 262 mass spectrometer. The reproducibility (2σ) of the isotopic measurements is 0.12% for $^{206}Pb/^{204}Pb$, 0.16% for $^{207}Pb/^{204}Pb$ and 0.22% for $^{208}Pb/^{204}Pb$. The repeated analyses of 15 galena samples were made at the University of Southampton by IsoProbe MC-ICP-MS using Tl-doping combined with sample-standard bracketing. Reproducibility on NBS 981 during the course of the measurement (2δ) is 16.942 ± 0.02%, 15.499 ± 0.02% and 36.725 ± 0.023% for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$, respectively: all are within error of accepted values. The U and Pb contents in whole ore and whole rocks samples were measured by ICP-MS (BRGM, Orléans). The lead isotopic ratios of whole rocks and ores were corrected for radioactive decay over 400 Ma using U and Pb contents.

4.2 Sm-Nd isotope analyses

The eight whole-rock samples were analyzed for their Sm-Nd isotope and elemental composition according to standard ion-exchange procedure at the Institut de Physique du Globe in Paris using a Neptune ICP-MS. Whole rock sample powder was spiked with a mixed ^{149}Sm-^{150}Nd tracer and dissolved using a 1:1 HF + HNO_3 mixture in a Teflon beaker. After evaporation, residues were dissolved in a mixture of 0.9 M boric and nitric acids. Separation of REE from the rock matrix was performed using TRU-Spec chromatographic columns. Nd and Sm were isolated from the other REEs using HDEHP Ln-Spec^{TM} extraction columns. The Sm and Nd residues were dissolved in 3% HNO_3 acid prior to the isotopic analyses carried out on a Neptune^{TM} multi-collector inductively coupled mass spectrometer (MC-ICP-MS) at the Institut de Physique du Globe in Paris (IPGP). The mean value of about 200 single measurements (10 blocks of 20 cycles) was used. The Nd Johnson and Matthey standard yielded $^{143}Nd/^{144}Nd$ = 0.511453 ± 20 (n=6, 2σ standard deviation) during the period of measurements; this corresponds to a value of 0.511840 ± 20 for the international Nd standard La Jolla. The Nd isotopic ratios were normalized to $^{146}Nd/^{144}Nd$ = 0.7219 using an exponential law and the total procedural blank was less than 5 pg for Nd.

5. Results

5.1. Lead isotope systematics

5.1.1 Ores

The lead isotopic compositions of galena (n=55), cerussite (n=1) and whole massive sulphide (n=5) samples show a range between 17.437 and 18.111 for $^{206}Pb/^{204}Pb$; 15.484 and 15.630 for

$^{207}Pb/^{204}Pb$ and 37.201 – 38.027 for $^{208}Pb/^{204}Pb$ (Table 1, Fig. 2). In the following, we describe the lead isotopic composition within different tectonic settings across the Southern Urals island arc.

The MUF suture zone. No galenas were found in three deposits situated within the mafic-ultramafic rocks in the tectonic melange that occupies the MUF suture zone. The samples investigated from the MUF suture zone consist of five massive and disseminated whole ore samples from the Ivanovskoye, Dergamish and Ishkinino deposits. The age corrected lead isotopic data for massive sulphide ores from the Ivanovskoye and Ishkinino deposits occur in an intermediate position on the $^{206}Pb/^{204}Pb$ versus $^{207}Pb/^{204}Pb$ diagram (Fig. 3, Table 2), close to the data cluster for the Alexandrinskoye and Sibay deposits. The coarse grained pyrrhotite samples show more radiogenic $^{207}Pb/^{204}Pb$ values (Fig. 3). These data are more radiogenic than that obtained by Vinogradov et al. (1960), probably the result of improvement in analytical techniques. The Dergamish deposit ores are characterised by the highest U and Pb contents and most variable decay corrected $^{206}Pb/^{204}Pb$ lead isotopic ratios (Table 2).

Magnitogorsk arc

West-Magnitogorsk island arc zone. The lead isotopic compositions were measured for 15 galena samples from six massive sulphide deposits hosted by the Baymak-Buribai Formation (Table 1, Fig. 2). The lead isotopic ratios are more radiogenic in the upper stratigraphy of the Baymak-Buribai Formation. The lower mafic boninitic-like sequence is host for the Oktiabrskoye deposit with the least radiogenic lead. The most radiogenic isotopic composition was recorded for the Baymak-type Balta-Tau deposit, which occurs at the contact between the Baymak-Buribai Formation and the overlying Irendik Formation (Herrington et al. 2002, Seravkin et al. 1994). The Urals-type Gai and Podolskoe giant deposits are hosted by the calc-alkaline Baymak-Buribai and Irendik Formations, respectively, and plot in an intermediate position in the $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ diagram (Fig. 2). The Bakr-Tau deposit shows the largest variations in all lead isotopic ratios (expressed as a difference between maximum and minimum values), exceeding analytical error (expressed after ± sign): 0.125±0.005 for $^{206}Pb/^{204}Pb$ ratio, 0.008±0.005 for $^{207}Pb/^{204}Pb$ ratio, and 0.105±0.01 for $^{208}Pb/^{204}Pb$ ratio (based on our data and data from Chernyshev et al., 2008). All other deposits clusters are very tight isotopic groups, and the data spread usually does not exceed the analytical error. Given that a large fractionation for lead isotope data from the Bakr-Tau deposit was found in the independent study by Chernyshev et al. (2008), this may be geologically significant.

Sibay inter-arc basin. The Urals-type Sibay deposit is characterised by the most radiogenic lead isotopic composition within the Magnitogorsk zone (Fig. 2). The model ages calculated according to the two-stage model of Stacey and Kramers (1975) is ca. 410±5 Ma, which is ~30 Ma older than the presumed Givetian biostratigraphic age (~380 Ma).

East-Magnitogorsk island arc zone. Three studied deposits (Uchaly, Molodezhnoye, and Alexandrinskoye) within the Eastern part of Magnitogorsk island arc have an intermediate lead isotopic composition and plot between less radiogenic Pb data for the Baymak-Buribai deposits, and more radiogenic lead of the Sibay deposit on the uranogenic diagram (Fig. 2). The lead isotopic data for 22 galena samples and one cerussite [$PbCO_3$] sample from the continental weathering zone above the Alexandrinskoye deposit show an extreme homogeneity within analytical error. The small Baymak-type Babarik deposit in the same region has a slightly less radiogenic lead isotopic signature. The much younger episode of lead deposition with Permian lead model ages (*ca*. 260-280 Ma) was recorded in the hanging wall of the Alexandrinskoye and Uchaly massive sulphide deposits.

Dombarovka back-arc zone. The Dzhusa and Barsuchii Log deposits are characterised by the most radiogenic $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios of all Urals VHMS deposits. Their model age is *ca.* 415± 28 Ma (Stacey and Kramers, 1975), which is ~30 Ma older than the biostratigraphic age of ore hosting rocks.

Sakmara allochthon

The lead isotopic composition of two galena samples from the Urals-type Yaman-Kasy deposit fits within the field of the deposits situated in the Magnitogorsk island arc between the more radiogenic Sibay deposit and slightly less radiogenic Baymak-type and Alexandrinskoye deposits (Fig. 2). The Yaman-Kasy ores two-stage model ages (Stacey and Kramers, 1975) range from 400 up to 450 Ma and not contradict to the biostratigraphic Llandoverian (Silurian) age for the ore hosting volcano-sedimentary rocks (Herrington et al. 2002).

5.1.2. Rocks

In order to reconstruct the source of lead in volcanogenic massive sulphide deposits, thirty two samples from ore hosting volcanic and sedimentary rocks have been studied for their lead isotopic composition (Table 2), including: the MUF suture zone; the Baymak-Buribai, Irendyk and Karamalytash Formations; the Mednogorsk ore region; and volcano-sedimentary rocks and plagiogranite massif within the Alexandrinskoye ore field. The lead isotopic ratios, corrected for U-decay over 400 Ma, are shown on the $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ diagram together with ore lead data for the VHMS deposits (Fig. 3). The range of age corrected lead isotopic ratios is also quite large: $^{206}Pb/^{204}Pb$ =17.25-17.96; $^{207}Pb/^{204}Pb$ = 15.48-15.56, and match those of the ores.

Anomalous age-corrected isotopic compositions ($^{206}Pb/^{204}Pb$ ratios ranging from 6.36 to 23.73; Table 2) were obtained for serpentinites and altered volcanic rocks from the MUF suture zone. Nevertheless, the isochron age for all analysed rocks and ores from the MUF zone shows the stratigraphically meaningful age of 396 ± 55 Ma. After excluding anomalous values, the lead isotopic compositions for the mafic-ultramafic rocks are characterised by a large range with the most radiogenic data ($^{206}Pb/^{204}Pb$ = 18.286 and $^{207}Pb/^{204}Pb$ = 15.597) representing an ultramafic cumulate near the Ivanovskoye deposit (Table 2). Basalts near the Dergamish ore deposit are less radiogenic and match the field of the ores and rocks of the Magnitogorsk island arc (Fig. 3, Table 2). In summary, the volcanic and sedimentary rocks in the MUF suture zone show an extremely heterogeneous lead isotopic composition, possibly due to various rock types in a melange zone as well as submarine alteration processes, or more recent U and /or Pb mobility due to weathering.

In general, the lead isotopic compositions of the volcanic rocks are similar to the ore lead in the same ore field, e.g. in the Sibay area (see Fig. 3). The andesite in the type section of the Karamalitash Formation (Karamalytash Mountain) has a less radiogenic lead isotopic composition, similar to that of the acid volcanic rocks from the Alexandrinskoye ore field.

The most complete dataset of ore-bearing volcanic and sedimentary rocks have been analysed from the Alexandrinskoye VHMS deposit ore field. Most of them yield values identical to the lead isotopic composition of the sulphide ores (Fig. 4). Only three samples of dacites from the Alexandrinskoye ore field, as well as one plagiogranite clast yield less radiogenic values (~0.36 lower in the $^{206}Pb/^{204}Pb$ ratios). These samples are characterised by relatively low lead contents (2.5-4 ppm) and high U/Pb ratios of about 0.3 (Fig. 5). The isotopic compositions of the Alexandrinskoye plagiogranite clast and the acid volcanic rocks plot close to the Bogachevskiy plagiogranite complex and the Baymak-Buribay hosted VHMS deposits on the $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ diagram (Fig. 3).

Data for the U-Pb concentrations of the volcanic rocks from our study were complimented from the literature (Herrington et al., 2002; Spadea et al., 2002). As can be seen on Fig. 5, the tholeiitic series (Sibay ore field and MUF deposits) are characterised by low lead contents and higher U/Pb ratios as compared to the calc-alkaline Baymak-Buribai Formation.

5.2 Sm-Nd isotope systematics

Eight samples were selected from the same batch of samples analysed for Pb isotopes. They include: one basalt sample from the Karamalytash Formation hosting the Sibay deposit; one serpentinite (altered peridotite) from the Ivanovskoye ore field situated within the Main Uralian Suture zone; the rest of the samples were collected from the Alexandrinskoye ore field, including dacite, basalt, fine-clastic sediment (pelite), gossan from the submarine oxidation zone above ore body, and two plagiogranite samples. The Sm and Nd contents range from 0.3 to 2.6 ppm and from 0.9 to 11.3 ppm respectively (Table 3). The ε_{Nd} value is highest for basalt from the Alexandrinskoye ore field (8.1), decreasing progressively towards basalt from the Karamalytash Formation hosting the Sibay deposit (7.7) and it is lowest in altered peridotite from the Ivanovskoye ore field (6.8).

6. Discussion

6.1 Variations in lead isotopic composition across the Uralian island-arc

The lead isotopic compositions of all studied VHMS deposits show a large scatter on both the $^{206}Pb/^{204}Pb$ – $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ – $^{208}Pb/^{204}Pb$ diagrams (Fig. 2). The variation in isotopic composition on the scale of the Urals province is 0.67 for $^{206}Pb/^{204}Pb$. Although this range is much greater than the isotopically homogeneous composition of the massive sulphide deposits in the Palaeozoic Iberian Pyrite Belt (Marcoux, 1998), it is comparable to that measured for modern VHMS deposits from the back-arc basins of the Pacific ocean (Fouquet and Marcoux, 1995), and smaller than that of the Miocene Kuroko VHMS deposits from Japan island arc (variation of 1.62 for $^{206}Pb/^{204}Pb$; Sato, 1975). The difference between the least radiogenic lead of the Oktiabrskoye and the most radiogenic lead of the Barsuchii Log deposits is eight times greater than the radiogenic in-growth of lead due to decay of U and Th at representative μ values during the time of VHMS formation (ca. 50 Ma), which would not be greater than 0.08 for $^{206}Pb/^{204}Pb$ and 0.06 for $^{207}Pb/^{204}Pb$. Similarly, the model ages calculated according to a two-stage model of Stacey-Kramers (1975) vary from Proterozoic in the fore-arc setting to Devonian in arc and back-arc settings.

The isotopic data from 16 VHMS deposits display a systematic increase in radiogenic lead isotopic compositions ($^{206}Pb/^{207}Pb$, $^{207}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$ and $\Delta^{207}Pb/^{204}Pb$) eastwards across the Urals paleo-island arc, from fore-arc with least radiogenic lead and lowest $\Delta^{207}Pb/^{204}Pb$, to the back-arc with the most radiogenic lead isotopic ratios and the highest $\Delta^{207}Pb/^{204}Pb$ (Fig. 6A; Table 4) and μ values (Fig. 7). This eastward increase in lead isotopic ratios, $\Delta^{207}Pb/^{204}Pb$ and μ values coincides with the build-up of the Urals island-arc cross-section to the east, with the Karamalytash Formation (hosting the more radiogenic lead deposits in an island arc setting), overlying the Irendyk Formation (host for the Balta-Tau deposit) and the Baymak-Buribai Formation (hosting the least radiogenic deposits in fore-arc setting). The most radiogenic deposits in back-arc setting are considered to be found within stratigraphically younger formations (Fig. 6B).

The most heterogeneous lead isotopic composition was observed within the relatively small Baymak-type polymetallic deposits hosted by the Baymak-Buribai Formation, with the Bakr-Tau deposit showing the largest variation in $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ isotopic ratios (0.125 and 0.105, respectively), and the Oktiabrskoye deposit showing the largest difference in $^{207}Pb/^{204}Pb$ isotopic ratios (0.015) while taking into account only high precision new (Table 1) and published data from Chernyshev et al (2008), which has a higher analytical uncertainty. The deposits within the Karamalytash Formation, including the giant Sibay deposit, are characterised by highly homogeneous lead isotopic compositions, within the analytical error. Overall variability in lead isotopic composition within the deposits hosted by the Baymak-Buribai Formation is much larger than that in the overlying Karamalitash formation, reaching 0.3 for $^{206}Pb/^{204}Pb$, and 0.04 for $^{207}Pb/^{204}Pb$ ratios. The Balta-Tau deposit has a more radiogenic lead isotopic composition relative to the rest of the deposits in the fore-arc setting, and following the tendency of increasing lead isotopic composition upwards in the stratigraphic sequence, it indirectly confirms its position within the overlaying Irendyk Formation (Herrington et al., 2005).

6.2 Identification of lead sources within the Uralian island arc system

The non-radiogenic lead isotopic composition of VHMS deposits in fore-arc and arc settings imply the presence of a cryptic reservoir within the island arc structure, presumably characterised by low-radiogenic $^{207}Pb/^{206}Pb$ ratios and low μ values, which may be represented by: (1) older subducted oceanic crust (Brown et al., 2006); (2) cryptic underlying crystalline blocks from an old adjacent continent (Ershov and Prokin, 1992); (3) Neoproterozoic (Riphean) platform sediments (Sundblad et al., 1996). In order to identify the relative probability of these potential lead sources in a budget of lead in Urals VHMS deposits and their host rocks, we will need to analyse the existing dataset (Tables 1 and 2).

The linear array on the $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ diagram (Fig. 2A) can be explained in terms of the plumbotectonic model (Zartman and Doe, 1981) by a mixture of two or more components with different source μ-values. In the context of this model, the ore-forming metals must have been leached from the surrounding volcanic and sedimentary host rocks and homogenised at the scale of the ore field or even of the metallogenic province (e.g., Tosdal et al. 1999). In other words, the isotopic composition of the lead in ores should reflect an average isotopic composition of lead in the host rocks sequence at the time of ore formation. As seen on Figures 3 and 4, the isotopic composition of sulphide ores reflects those of host rocks, with the tholeiitic basalt in the Sibay ore field being more radiogenic than calc-alkaline volcanic rocks and plagiogranites from the Baymak-Buribai and Irendyk Formations. Interestingly, the felsic rocks from the Alexndrinskoye ore field are less radiogenic compared to associated basalts, and resemble those from the Baymak-Buribai and Irendyk Formations. The difference in lead isotopic composition between the sulphide ores and felsic rocks from the same ore field may be due to low lead contents in the felsic rocks (≥4 ppb) compared to basalts (up to 4.8 ppm). However, two metasomatised dacite samples from the same ore field have high lead contents (43 and 60 ppb) and isotopic composition similar to that of basalts. It possibly means that not all felsic rocks were affected by hydrothermal fluid flow and preserve their original isotopic composition. If the composition of felsic rocks reflects the composition of their source, this is clear evidence concerning the nature of the low-radiogenic component.

The origin of felsic rocks in intra-oceanic arc setting is still a matter of debate (e.g., Haase et al., 2011), with major models describing their formation either by extreme fractional crystallisation of mafic magma, or by partial melting of older mafic crust. The former model is not supported by the difference in isotopic composition among the basalts and felsic volcanics from the same ore field (Fig. 4, Table 2), giving more credibility to the latter model. The partial melting of older subducted oceanic crust may be a potential source of lead in the intra-oceanic Magnitogorsk island arc setting.

6.2.1 Ordovician MORB mantle

Lead isotopic compositions of the Ordovician MORB from the Urals (Spadea and d'Antonio, 2006) are similar to those of deposits in the MUF zone, as well as deposits in back-arc (Dzhusa and Barsuchii Log) and rifted arc (Sibay) settings (Fig. 7B). The Uralian MORBs are much more radiogenic compared to the average composition of MORB and oceanic basalts in Northern hemisphere (Hart, 1984), which is represented by the Northern Hemisphere Reference Line (NHRL; Figs 2 and 3). This difference may be quantified using the $\Delta^{207}Pb/^{204}Pb$ parameter, which is expected to be close to zero for the majority of depleted mantle derived rocks in the Northern Hemisphere (Hart, 1984). The $\Delta^{207}Pb/^{204}Pb$ of Uralian MORBs is as high as 11 (using the data from Spadea and d'Antonio, 2006), showing a clear enrichment in radiogenic lead. This enrichment in Urals MORB and peridotites has been ascribed to the variable contributions from a sedimentary component likely made up of pelagic clays (Spadea and d'Antonio, 2006), with most of the data showing intermediate composition between typical MORB and oceanic sediments.

The initial lead isotopic compositions of three deposits within the MUF zone, namely Degamish, Ivanovskoye and Ishkinino (Table 2), are comparable to that of the Ordovician MORBs from the Urals (Spadea, d'Antonio, 2006), as well as some sulphide deposits in the back-arc and rifted arc region (Sibay, Barsuchii Log, Dzhusa). The calculated two-stage lead model ages for these deposits are close to the age of the volcanics (~400 Ma). The lead isotopic composition of the giant Sibay deposit ores in a rifted arc setting matches those of Ordovician MORB most closely (Fig. 3). The Sibay ore-hosting tholeiitic volcanics are characterised by high titanium and low lead contents, with high U/Pb ratios. The available REE data indicates a depleted MORB-type source for the Sibay deposit, similar to that of the mafic-ultramafic rocks from the MUF suture zone (Herrington et al. 2002). Least radiogenic lead isotopic compositions of mafic-ultramafic rocks within the MUF suture zone is similar to that of Ordovician MORB, with some anomalous ratios, which may be the result of high-grade submarine alteration with subsequent U release, clearly indicating open system behaviour for the lead isotopes, or more recent U-Pb mobility due to weathering. Recent geological and geochemical studies indicate a supra-subduction setting for the deposits in the MUF suture zone and their hosting mafic-ultramafic rocks, formed at shallow depth with addition of subduction-related fluids (Tesalina et al., 2003; Nimis et al., 2008). This metasomatic process should also affect lead isotopic compositions, introducing radiogenic lead from subducted sediments and altered oceanic crust into the mantle wedge.

Thus, the similarity of lead signatures in the rifted arc and back-arc related deposits as compared to that of Ordovician MORBs (Fig. 7B), suggests that the origin of their host rocks was by the partial melting of metasomatized depleted mantle. In contrast, deposits in fore-arc and mature arc settings are considerably less radiogenic (Table 1 and 2), indicating contributions from less radiogenic, and therefore presumably older, components.

6.2.2 Proterozoic mafic-ultramafic rocks

The presence of older Neoproterozoic mafic-ultramafic rocks within the Urals orogen is shown by a number of recent studies (e.g., Tessalina et al., 2007; Ronkin et al., 1997, 2009, 2012; Maegov, 2008; Efimov et al., 2010; Popov and Belyatsky, 2006; Petrov et al, 2010). These studies report Proterozoic Sm-Nd and Re-Os isochron ages for mineral separates and whole rocks from a number of mafic-ultramafic massifs (Fig. 9). These ages range from Mesoproterozoic (1250±80; Tessalina *et al*., 2007) to Neoproteroziuc (871±53 Ma, Malitch et al.; 882±83 and 804 ±37 Ma, Tessalina et al., 2007) and Neoproterozoic – Ediacaran (540-560 Ma; Ronkin et al., 1997, 2009, 2012; Maegov, 2008; Efimov et al., 2010; Popov & Belyatsky, 2006; Petrov et al, 2010), which coincides with the Timanian orogeny (Puchkov, 2010) and precedes the formation of crust in the Paleo−Uralian ocean. Interestingly, several workers (e.g., Samygin et al., 2010; Samygin and Burtman, 2009) consider that the formation of the Uralian Ocean inherited the older Neoproterozoic Ocean, which seems to be supported by this ‘old’ isotopic dataset. The Neoproterozoic ages are especially prominent for a number of mafic-ultramafic peridotites and volcanics (Fig. 9; Samygin and Burtman, 2009), which coincide with model Pb ages (Tables 1 and 2) of studied VHMS deposits. The partial melting of these mafic-ultramafic assemblages during the reactivation of Uralian paleoocean would potentially explain the low radiogenic composition of VHMS deposits and ore hosting rocks of Baymak-Buribai Formation, and the felsic rocks from the Alexandrinskoye ore field. This reactivation is also supported by multi-stage evolution of several Urals mafic-ultramafic massifs (Tessalina et al. 2007; Savelieva et al. 2007), with younger melting events corresponding to the development of Palaeozoic Uralian paleoocean.

6.2.3 Archean continental crust

Possible contribution from an older crustal component was proposed in previous works based on lead isotopic composition of galena from Urals massive sulphide deposits (Ershov and Prokin, 1992; Sundblad et al., 1996; Brown and Spadea, 1999). Considering that the old continental rocks/sediments may represent an alternative source of lead, one can estimate the approximate age of this older component on $^{206}Pb/^{204}Pb$ vs $^{207}Pb/^{204}Pb$ diagram. Doing this for all studied deposits in

Southern Urals, we come up with an age of 2.70±0.15 Ga (MSWD=3.4, Model 2 fit in Isoplot, Fig. 8A). This age coincides with oldest Neoarchaean (2,781 ± 56 Ma) ages established for the zircons extracted from some of the Urals peridotites (Malitch *et al*., 2009; Fershtater *et al*., 2009).

The similarity of lead isotopic composition between the massive sulphide deposits of Baymak type (Table 1: Oktiabrskpye, Bakr-Tau, Tash-Tau, Balta-Tau and Uvariazh) and their host rocks of Baymak-Biribai and Irendyk Formations (Table 2, Fig. 3) imply that the lead was mainly derived from ore-hosting rocks, in agreement with a recycling model. If this distinct lead isotopic signature depends on the contribution of older continental crust, it would also influence other isotope systematics, especially composed of lithophile elements (e.g., Sm-Nd), which are sensitive to crustal contamination. The Nd isotopic composition of volcanics from Baymak-Buribai Formation has been reported in previous works (e.g., Spadea and d'Antonio, 2006), with the published ε(410)Nd values ranging from 3.4 to 6.8, with an average of 5.7. This average value corresponds to our measured ε(400)Nd for plagiogranite from the Baymak-Buribai Formation (5.7; Table 3). These values are *ca*. 3 εNd units lower than that of Ordovician MORBs (Spadea and d'Antonio, 2006), which may be explained by some extent of crustal contamination (older crust is characterised by low εNd values). The extent of continental crust/sediments contribution towards the arc-related volcanism may be estimated using a mixing model with new and published Nd and Pb isotopic compositions (Fig. 10). Model continental crust compositions may be approximated using the Nd isotopic compositions of Archean rocks from the Volga-Uralia Craton (Table 5; Bibikova et al., 2009), whereas model Urals depleted mantle may be taken from the data of Spadea and d'Antonio (2006). Figure 10 shows that very little contribution of continental crustal rocks is needed (less than 1%) to reproduce the measured isotopic composition of the least radiogenic rocks and ores.

6.2.4 Neoproterozoic platform sediments

Another reservoir, which has been previously considered as a possible source of the 'old' lead signature, constitutes the Neoproterozoic platform sediments (Sunblad et al., 1996). These sediments have been developed on the margins of the East-European craton within the epicratonic riftogenic-depressional sedimentary basins. Fragments of such sediments are still preserved within the Bashkirian anticlinorium adjacent to the Main Uralian Fault zone (Fig. 1). This anticlinorium is hosting the Bakal iron minetralization within the terrigenous and carbonate deposits of the Bakal Formation, dated at 1,430±30 Ma (Kuznetsov et al., 2005). Galena from this deposit is characterised by a low μ value of 8.8 and high $\Delta^{207}Pb/^{204}Pb$ value of 20.1 (Table 1; Fig. 7). However, this component has a high $^{207}Pb/^{204}Pb$ ratio, and alone cannot account for the generation of the lead isotopic signature of VHMS deposits in the fore-arc setting, requiring an additional component with low $^{207}Pb/^{204}Pb$ ratio. Given that the Urals MORB mantle in Ordovician times was contaminated by a radiogenic component, it could not balance the composition of Proterozoic sediments to obtain the 'intermediate' composition of VHMS sulphides. In light of these considerations, this component alone is considered to be unlikely as a main source of 'old' lead.

7.3 Implication for geodynamic development

The Urals Ordovician MORBs may be considered as analogous of subducted oceanic crust and characterised by radiogenic lead isotopic compositions (Spadea and d'Antonio, 2006), similar to that of back-arc and rifted-arc volcanics and VHMS deposits, but do not explain the non-radiogenic lead values of other studied deposits. However, the multi-stage history of several Uralian mafic-ultramafic massifs began in Neoproterozoic time, which coincides with Neoproterozoic Pb model ages of VHMS deposits. The presence of a Neoproterozoic tectono-magmatic event was considered by a number of workers based on Neoproterzoic ages of zircons extracted from Urals ophiolites (e.g., Savelieva et al., 2007); Re-Os and Sm-Nd ages of several dunite-clinopyroxenite massifs (e.g., Tessalina et al., 2007; Ronkin et al., 1997, 2009, 2012; Maegov, 2008; Efimov et al., 2010; Popov and Belyatsky, 2006; Petrov et al, 2010); and Neoproterozoic ages of volcanic and intrusive rocks on the western slope of Urals with ages ranging from ca 700 Ma to 515 Ma (Samigin and Rugenzev, 2003). These prominent Neoproterozic ages have been interpreted by some workers (e.g., Samygin and Burtman, 2009) as evidence for the inherited character of the Urals paleo-ocean, which started in the Neoproterozoic with development of the earlier pre-Uralian island arc system. This model will explain the older

Neoproterozic model ages of studied deposits. However, the presence of older mafic-ultramafic massifs within the Palaeozoic Uralian Ocean may also be due to the subsistence of subcontinental lithospheric mantle fragments during the rifting of Laurussia continent, as demonstrated, among other sites, beneath the extended margin of the Southern China block in the Taiwan Strait (e.g., Wang et al., 2003).

Another possibility could be the influence of old continental crust fragments present in the basement of the intra-oceanic arc, a scenario that has recently been shown in modern intra-oceanic arcs of Vanuatu (Buys et al., 2014) and the Solomon Islands (Tapster et al., 2014). The remnants of older crustal fragments in these two settings has been demonstrated by the presence of old Archean zircons. Archean and Proterozoic zircons have also been extracted from Urals peridotites (e.g., dunites within a number of dunite-clinopyroxenite massifs), with U-Pb ages ranging from Neoarchaean (2,781 ± 56 Ma), Paleoproterozoic (2,487 ± 33 Ma and 1,881 ± 9 Ma), Mesoproterozoic (1,172 ± 9.8 Ma) to Mid-Paleozoic (414.8 ± 3.9 – 473 ± 3.7 Ma), reflecting the multistage formation history of the Uralian Platinum Belt (Malitch *et al*., 2009; Fershtater *et al*., 2009). These Archaean zircons are consistent with source from the East-European craton, or, more precisely, from Volga-Uralia block, adjacent to the Urals orogenic belt, which has been formed as a result of the Neoarchean plume event at 2.74-2.6 Ga, transforming earlier Archaean continental crust (3.4-3.0 Ga) (Mints, 2011).

The two-stage model age for all South Urals VHMS deposits is ~2.7 Ga (Fig. 8A), which is close to that of the Volga-Uralia Craton (2.74-2.6 Ga; Mints, 2011). In the modern Urals structure, an Archean-Proterozoic sequence is present under the Southern and Middle Urals Palaeozoic structures as a continuation of the East-European craton. Inside the Urals structure, Archean rocks (average zircon U-Pb age of 2.9±0.2 Ga) are exposed within the Taratash uplift (Puchkov, 2010). The similarity of model Pb-Pb age established for all Southern Urals VHMS deposits with the age of adjacent Archean continent, together with the presence of old Archean zircons within Urals peridotites, support the possibility of old continental crust fragments being present in the base of the Uralian island arc.

The influence of this older oceanic or continental crust component is progressively less both upwards through the stratigraphic succession and with increasing distance from the subduction front, becoming almost nil in the rifted arc and back-arc settings, as shown by the progressive decrease in μ values up the stratigraphic cross-section (Fig. 11, Table 4). This may suggest that these continental fragments (i) were present during the intra-oceanic stage of Urals development in the form of fragments of older Neoproterozic oceanic crust or Archean continental crust from the adjacent East-European craton; or (ii) were introduced via the subduction zone much earlier than previously thought. The presence of continental fragments within the intra-oceanic arc structure was demonstrated recently under the example of two modern island arcs (Buys et al., 2014; Tapster et al., 2014). It has been suggested that these fragments have been rifted and transported thousands of kilometres away from the source continent (Buys et al., 2014). The possibility of this scenario in Urals is indirectly confirmed by the presence of old zircons within peridotite massifs (e.g., Malitch et al., 2009; Fershtater et al., 2009). The involvement of Neoproterozoic oceanic crust is also plausible and would explain the non-radiogenic isotopic composition by melting of Neoproterozoic subducted oceanic crust shortly after initiation of Urals development, explaining Neoproterozoic Pb model ages and mantle-like characteristics inferred from other isotope systematics (Nd-Sr; Spadea and d'Antonio, 2006), as well as 'enriched' Δ^{207}Pb values compare to average Northern Hemisphere Reference Line.

Another scenario implies the development of island arc volcanism after the subduction of older continental blocks and/or sediments that contradicts the existing dating of subduction processes. According to recent ^{40}Ar/^{39}Ar, U-Pb, and Sm-Nd isotopic data from eclogite in the Lower Unit of the Maksyutov Complex, the high-P eclogite-facies metamorphism occurred about 380 Ma ago (Givetian – Eifelian) during the eastward subduction of the East European craton beneath the Magnitogorsk island arc (Glodny et al. 2002), which postdates the formation of the Baymak-Buribay Formation during Emsian times (407-398 Ma). The timing of collision of this volcanic arc with the adjacent Laurussia continent has been established at 380-372 Ma, based on Ar-Ar, U-Pb and Sm-Nd dating of high-pressure metamorphic rocks and sediments belonging to the continental margin (Glodny et al., 2002). The formation of Southern Urals Volcanogenic Massive Sulphide deposits was restricted to the intra-oceanic stage, with a youngest age of 385 Ma based on biostratigraphic studies of ore-hosting volcanic and sedimentary rocks (Herrington et al., 2002).

Conclusions

The lead isotopic compositions of galenas, sulphide ores and whole rocks have been studied for 16 Urals VHMS deposits. The results show a systematic trend with the lead of the Sibay, Barsuchii Log and Dzhusa deposits being most radiogenic by comparison with those of Bakr-Tau and Oktiabrskoye which are the least radiogenic deposits. The Bakr-Tau and Oktiabrskoye deposits occur within the most primitive fore-arc rocks at the lower part of the Baymak-Buribai Formation, which contain lavas of boninitic affinity. The Sibay, Barsuchii Log and Dzhusa deposits are found in intra- and back-arc settings and are hosted by a sequence of bimodal tholeiites. The deposits in “arc” settings such as the Balta-Tau, Gai and Alexandrinskoye deposits occupy an intermediate position.

Low radiogenic ‘old’ signatures decrease from the fore-arc to the arc setting, and become almost nil in the back-arc setting. In general, the isotopic composition of lead resemble that of the host volcanics, with the exception of felsic volcanics and plagiogranite from the Alexandrinskoye ore field being less radiogenic compare to the basaltic part of the cross-section. Such a scenario would imply a different source for the melts generating the felsic volcanics in this setting. This source may be represented by older Neoproterozic oceanic crust, already demonstrated by multiple Neoproterzoic ages recorded for mafic-ultramafic massifs across the Urals. The relics of these massifs have been attributed to belong to earlier Neoproterozoic stages of pre-Uralian ocean development. Alternative sources of lead may be old Archean continental crust fragments or sediments sourced from the adjacent East-European continent, or Proterozoic sediments accumulated near the adjacent continent and presently outcropping near the western edge of Urals (Bashkirian anticlinorium). The contribution of Archean rocks/sediments to the Urals volcanic rock formation is estimated to be less than 0.1% based on Pb-Nd mixing model.

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FIGURES LEGEND

Figure 1. Simplified geological map of the Southern Urals showing the main regions of arc volcanic sequences and location of studied VHMS deposits (after Herrington et al. 2005 and references therein). Massive sulphide deposits: 2 – Yaman-Kasy, 3 – Oktyabrskoye, 4 – Bakr-Tau, 5 – Balta-Tau, 6 – Tash-Tau and Uvariazh, 7 – Gai, 8 – Podolskoye, 9 – Sibay, 10 – Molodezhnoye, 11 – Uchaly, 12 – Alexandrinkoye and Babarik, 13 – Dzhusa, 14 – Barsuchii Log, 15 – Ivanovskoye and Dergamish, 16 – Ishkinino. The Bakal iron deposit is situated within Proterozoic rocks of the Bashkirian anticlinorium (1). Sayreyskoye Pb-Zn sulphide-barite deposit is situated in the Polar Urals (17).

Figure 2. (top) $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ and (bottom) $^{206}Pb/^{204}Pb$ vs. $^{208}Pb/^{204}Pb$ diagrams for studied Urals massive sulphide deposits (Table 1), subdivided after their tectonic settings. The analytical precisions (2δ) are shown in the upper left corner for TIMS Pb isotopic data (corrected for mass fractionation by constant-f [f = c]; rho $^{207}Pb/^{204}Pb$ – $^{206}Pb/^{204}Pb$ = 0.999; rho $^{208}Pb/^{204}Pb$ – $^{206}Pb/^{204}Pb$ = 0.999) produced in BRGM (large ellipse); contained within the smaller ellipse represents Tl-spiked data produced in University of Southampton using MC-ICPMS (rho $^{207}Pb/^{204}Pb$ – $^{206}Pb/^{204}Pb$ = 0.938; rho $^{208}Pb/^{204}Pb$ – $^{206}Pb/^{204}Pb$ = 0.921; Taylor et al., 2015). The crosses represent lower precision TIMS analytical data. The high-precision data produced by MC-ICPMS with the addition of a Tl-spike are shown in a legend for each deposit. The data from Oktiabrskoye and Bakr-Tau deposits are complemented by Tl-spiked high-resolution data from Chernyshev et al. (2008). Red line represents the Northern Hemisphere Reference line (NHRL), representing a common trend for most of the MORB and Ocean Island basalts in the Northern hemisphere (Hart, 1984).

Figure 3. $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ diagram for volcanic and sedimentary rocks and sulphide ores from the Main Uralian Fault Zone (including the Ivanovskoye, Ishkinino and Dergamish deposits); Karamalitash formation (Alexandrinskoye and Sibay ore fields and Karamalitash Mts. cross-section), and plagiogranite massifs from Baymak-Buribai formation (Table 3). The galenas from the Urals VHMS deposits are shown for comparison. All data are corrected for decay over 400 Ma using measured U contents (Table 2). Orogen and mantle lead evolution curves are taken from Zartman and Doe (1981).

Figure 4. $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ diagram for the Alexandrinskoye ore field volcano-sedimentary rocks, corrected for U-decay over 400 Ma, in comparison with galena from sulphide ores. Most of volcanic and sedimentary rocks are identical to the sulphide ores in their lead isotope composition. Some felsic rocks (3 dacites and plagiogranite clast) are less radiogenic for both $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios. Error is similar to what is shown on Fig. 2.

Figure 5. Pb vs. U/Pb diagram for Urals volcano-sedimentary rocks (data from Herrington et al., 2002; Spadea et al., 2002 and this study). The tholeiitic series in fore-arc and rifted arc settings (MUF zone and Sibay ore field) are characterised by low lead contents and high U/Pb ratios compared to tholeiitic and calc-alkaline Baymak-Buribai series in fore-arc and arc settings.

Figure 6. Variation in $\Delta^{207}Pb/^{204}Pb$ with longitude (top) and stratigraphic age position in cross-section (bottom). The $\Delta^{207}Pb/^{204}Pb$ was defined by Hart (1984) as percentage deviations of $^{207}Pb/^{204}Pb$ from the Northern Hemisphere Reference Lines (NHRL). Longitude data for VHMS deposits were taken from the USGS dataset for Volcanogenic massive sulphide deposits of the world: http://mrdata.usgs.gov/. The legend for deposits is the same as on Fig. 2. The stratigraphic cross-section of the Southern Urals showing the ore-bearing formations is taken from Herrington et al (2005).

Figure 7. (A) The 2-stage model age for all South Urals VHMS deposits using only high-resolution data (model 2 fit in Isoplot); (B) $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ diagram showing the lead isotopic compositions of studied VHMS deposits along with Ordovician Mantle and Ordovician sediments fields. Non double spike data is expressed as average isotope ratios for each VHMS deposit, while individual double spike lead isotopic data are plotted. Ordovician MORB Mantle was delineated using data from Spadea and d'Antonio (2006). The Ordovician sediment field corresponds to the galena from the Ordovician sediments-hosted Saureyskoe Zn-Pb deposit, Polar Urals (Fig. 1). The lead isotope composition of (Fig. 1) sediments (~1.4 Ga) from Bakal stratiform iron deposit (Bashkirian anticlinorium) is shown. The average isotopic composition of Iberian Pyrite Belt (IPB) sulphides are shown for comparison.

Figure 8. Model two-stage μ values against the longitude for Urals VHMS deposits. The data for VHMS deposits from Tagil Arc (Middle Urals) are also shown (Chernyshev et al., 2006).

Figure 9. Comparison of lead model ages for ores and rocks with that of U-Pb ages of zircons recovered from Urals peridotites (Malith et al., 2009; Fershtater et al. 2009), and Neoproterzoic ages of peridotites established by Sm-Nd and Re-Os methods (Tessalina et al., 2007; Ronkin et al., 1997, 2009, 2012; Maegov, 2008; Efimov et al., 2010; Popov & Belyatsky, 2006; Petrov et al, 2010). Major tectonic events are also shown, referring, amongst others, to the Volga-Uralia Craton (2.74 Ga, Mints, 2011), Urals MOR formation (0.472 Ga) and subduction (0.407 Ga).

Figure 10. Mixing model on μ - ε(400)Nd plane. The end-members compositions are given in a Table 5. The Pb-Nd elemental and isotopic data for the Urals depleted mantle are taken from Spadea and d'Antonio (2006). The Nd composition for the Archean continental crust (Volga-Uralia craton) is taken from Bibikova et al (2009); whereas the Pb isotopic composition for Proterozoic continental crust is taken from this work (Table 1). Where the data are not available, the model parameters are used.

Figure 11. Schematic model for the Southern Urals after arc-continent collision (modified after Brown and Spadea, 1999) with corresponding model μ-values for deposits in different settings. Entering of Proterozoic rocks into subduction zone caused high-pressure metamorphism accompanied by release of fluid. This fluid provoked hydrous melting in the overlying mantle wedge. The lead isotopic composition of Proterozoic rocks is characterised by low model μ-values. In fore-arc settings, the model μ-values of VHMS deposits is close to that of Proterozoic rocks. Farther to the mature arc setting, the model μ-value progressively increases, with a maximum value of ~9.4. In back-arc settings, the anhydrous decompressional melting of oceanic crust prevails, with the highest μ-values corresponding to that of Ordovician crust (~9.6).

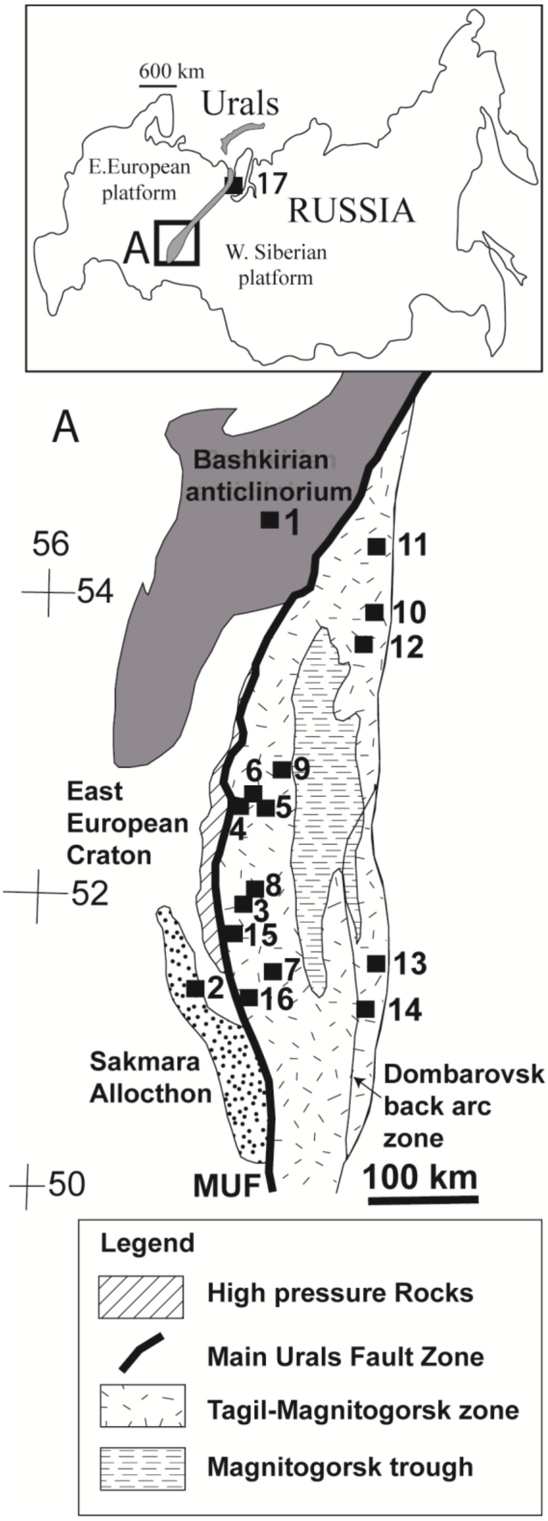
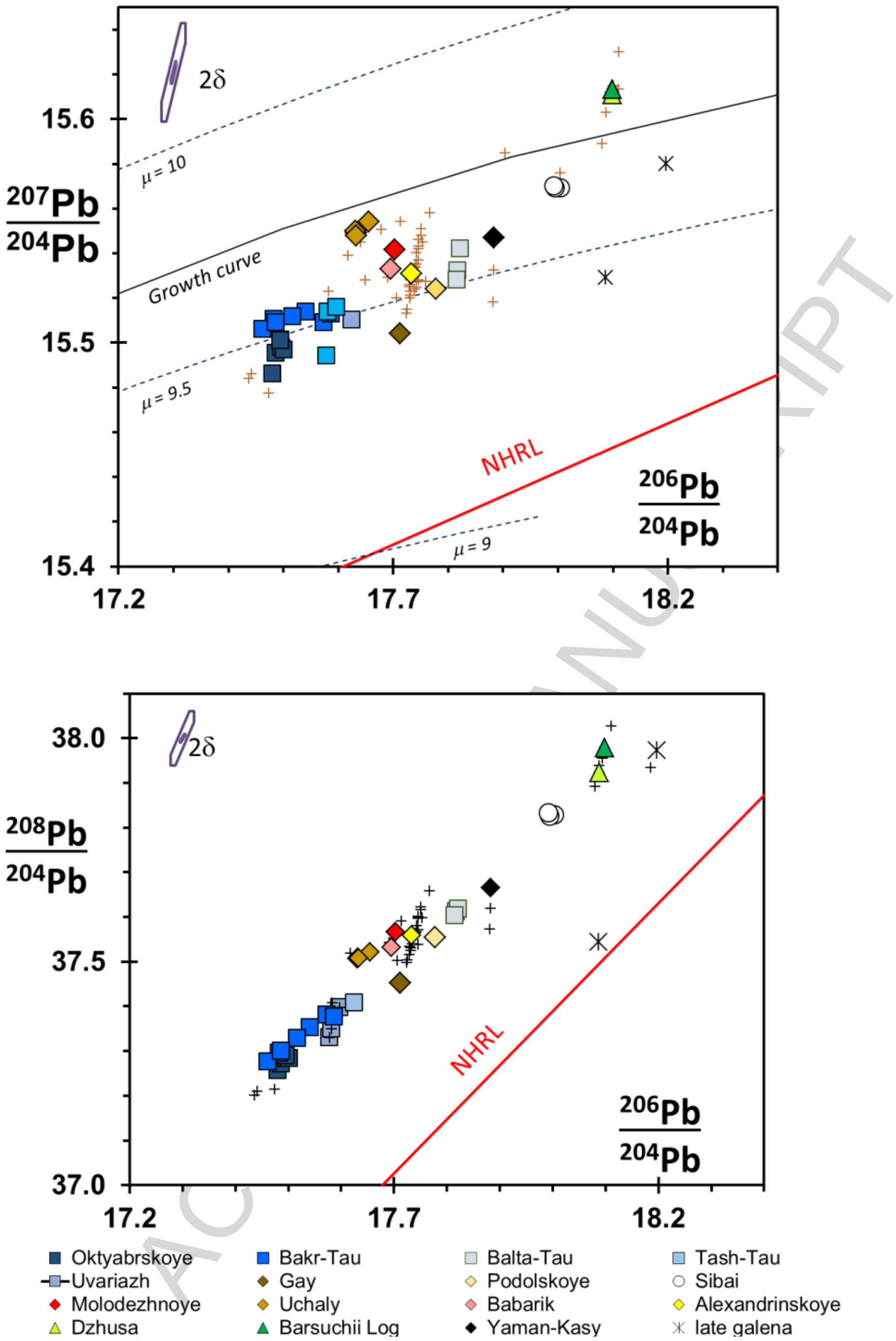

600 km
Urals
E.European platform
17
RUSSIA
A
W. Siberian platform
A
Bashkirian anticlinorium
1
56
54
11
10
12
6
9
5
4
East European Craton
52
8
3
15
7
2
16
13
14
Sakmara Allocthon
Dombarovsk back arc zone
50
MUF
100 km
Legend
High pressure Rocks
Main Urals Fault Zone
Tagil-Magnitogorsk zone
Magnitogorsk trough

Fig. 1.



15.6
15.5
15.4
17.2
17.7
18.2
$^{207}Pb/^{204}Pb$
$^{206}Pb/^{204}Pb$
2δ
μ = 10
μ = 9.5
μ = 9
Growth curve
NHRL
38.0
37.5
37.0
$^{208}Pb/^{204}Pb$
Oktyabrskoye
Uvariazh
Molodezhnoye
Dzhusa
Bakr-Tau
Gay
Uchaly
Barsuchii Log
Balta-Tau
Podolskoye
Babarik
Yaman-Kasy
Tash-Tau
Sibai
Alexandrinskoye
late galena

Fig. 2.

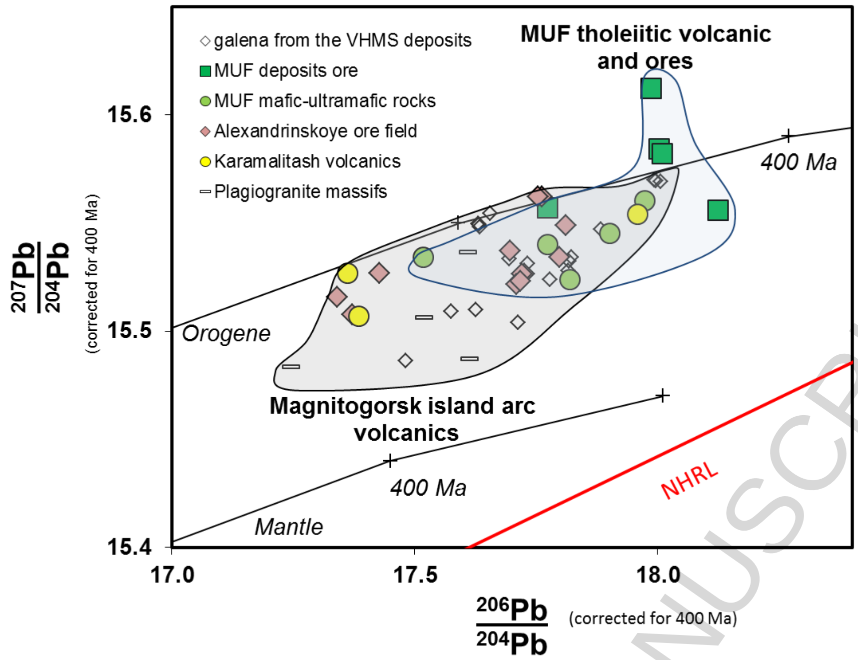

galena from the VHMS deposits
MUF deposits ore
MUF mafic-ultramafic rocks
Alexandrinskoye ore field
Karamalitash volcanics
Plagiogranite massifs
MUF tholeiitic volcanic and ores
400 Ma
Orogene
Magnitogorsk island arc volcanics
400 Ma
NHRL
Mantle
15.6
15.5
15.4
17.0
17.5
18.0
207Pb/204Pb
(corrected for 400 Ma)
206Pb/204Pb
(corrected for 400 Ma)

Fig. 3.

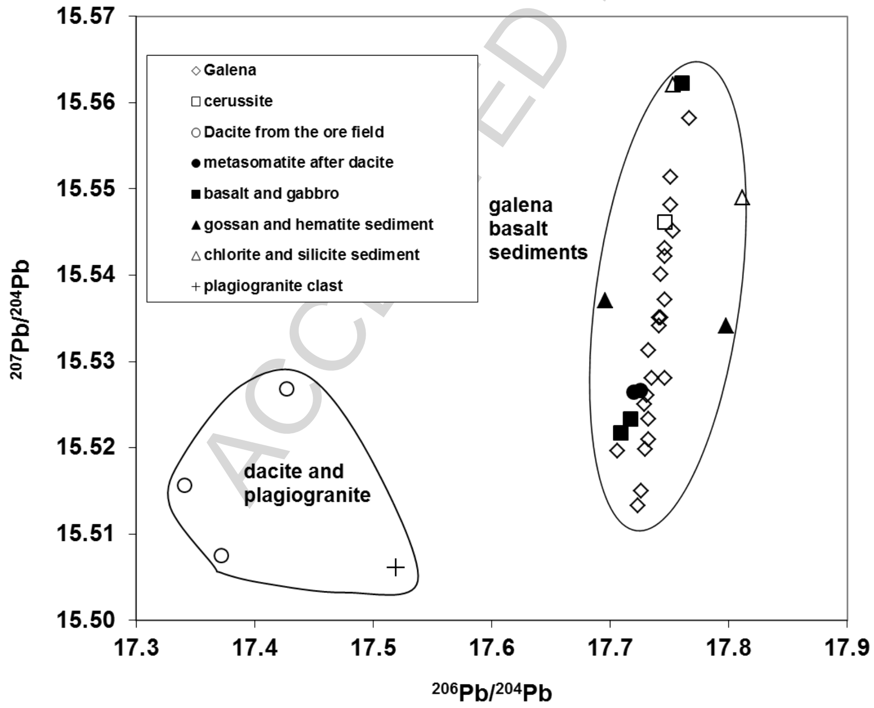
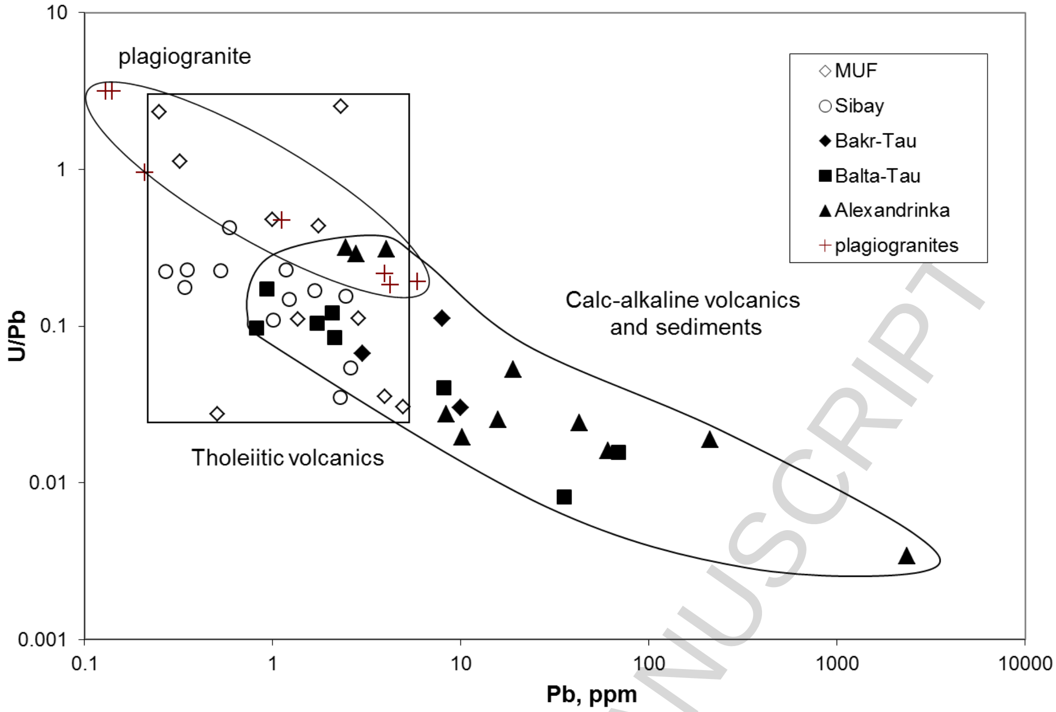
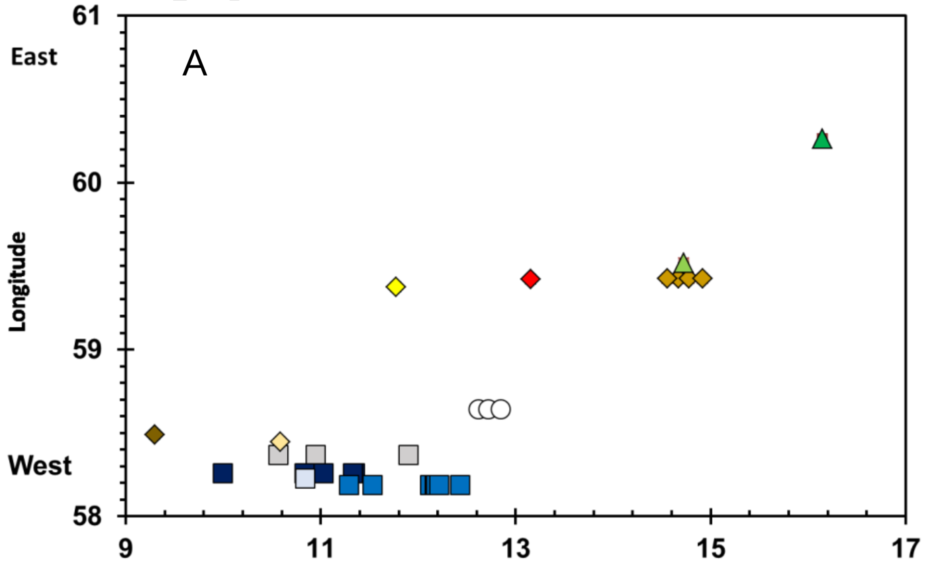

Galena
cerussite
Dacite from the ore field
metasomatite after dacite
basalt and gabbro
gossan and hematite sediment
chlorite and silicite sediment
plagiogranite clast
galena
basalt
sediments
dacite and
plagiogranite
15.57
15.56
15.55
15.54
15.53
15.52
15.51
15.50
17.3
17.4
17.5
17.6
17.7
17.8
17.9
207Pb/204Pb
206Pb/204Pb

Fig. 4.

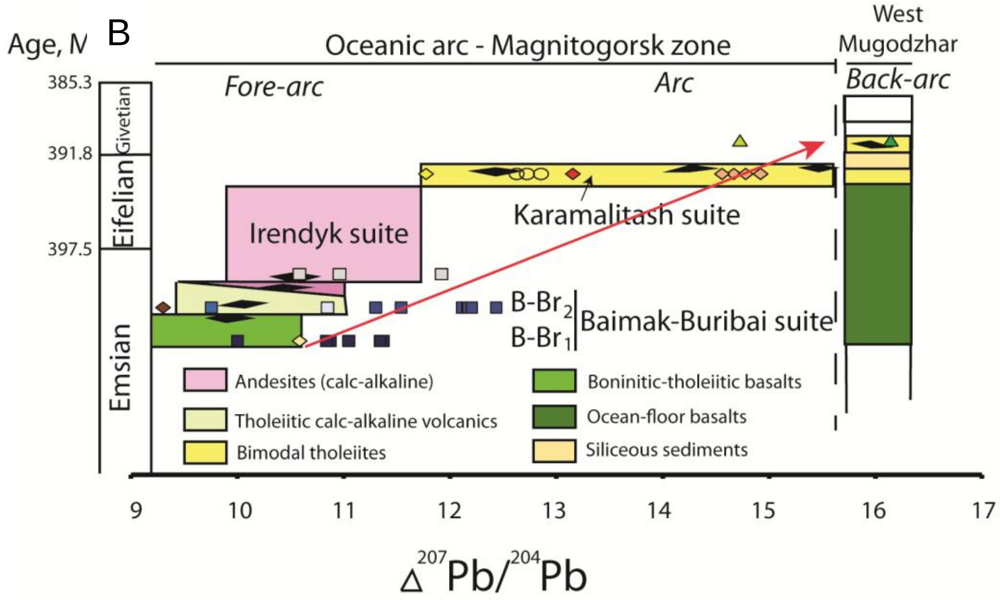


plagiogranite
MUF
Sibay
Bakr-Tau
Balta-Tau
Alexandrinka
plagiogranites
Calc-alkaline volcanics and sediments
Tholeiitic volcanics
U/Pb
Pb, ppm
10
1
0.1
0.01
0.001
0.1
1
10
100
1000
10000

Fig. 5.

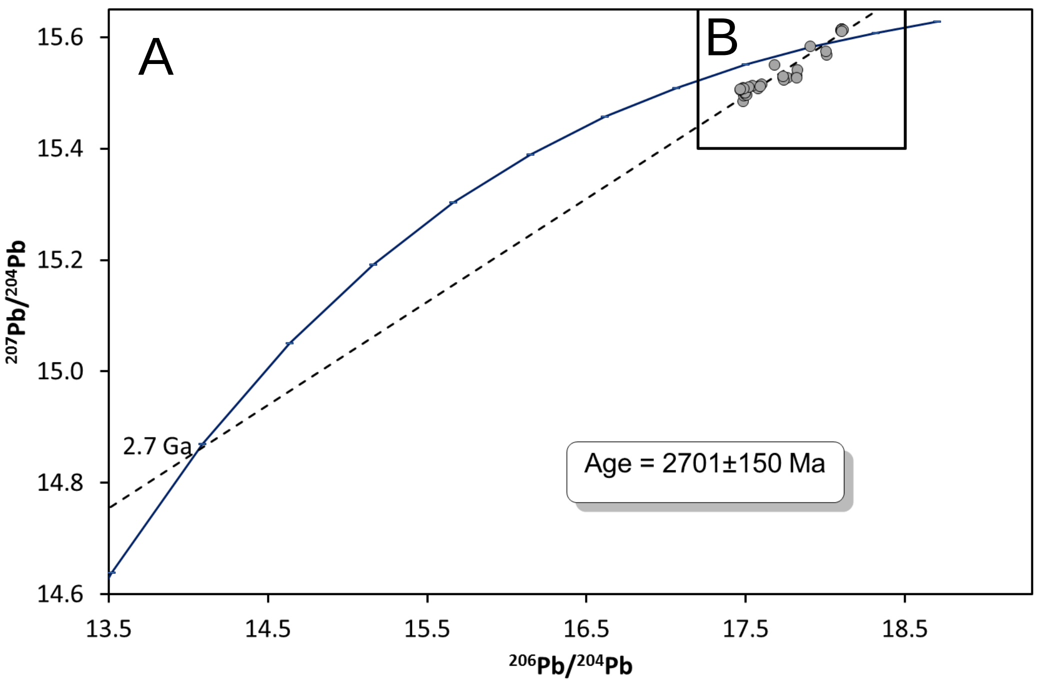


A
East
West
Longitude
61
60
59
58
9
11
13
15
17

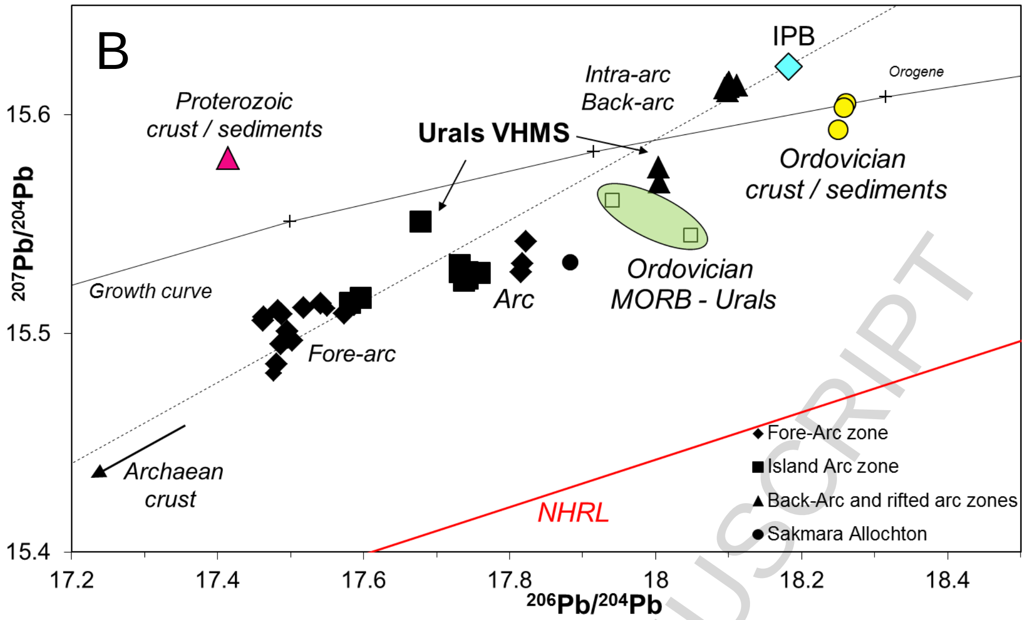


B
Age, M
Oceanic arc - Magnitogorsk zone
West Mugodzhar
Fore-arc
Arc
Back-arc
385.3
391.8
397.5
Givetian
Eifelian
Emsian
Irendyk suite
Karamalitash suite
B-Br2
B-Br1
Baimak-Buribai suite
Andesites (calc-alkaline)
Tholeiitic calc-alkaline volcanics
Bimodal tholeiites
Boninitic-tholeiitic basalts
Ocean-floor basalts
Siliceous sediments
9
10
11
12
13
14
15
16
17
Δ207Pb/204Pb

Fig. 6.

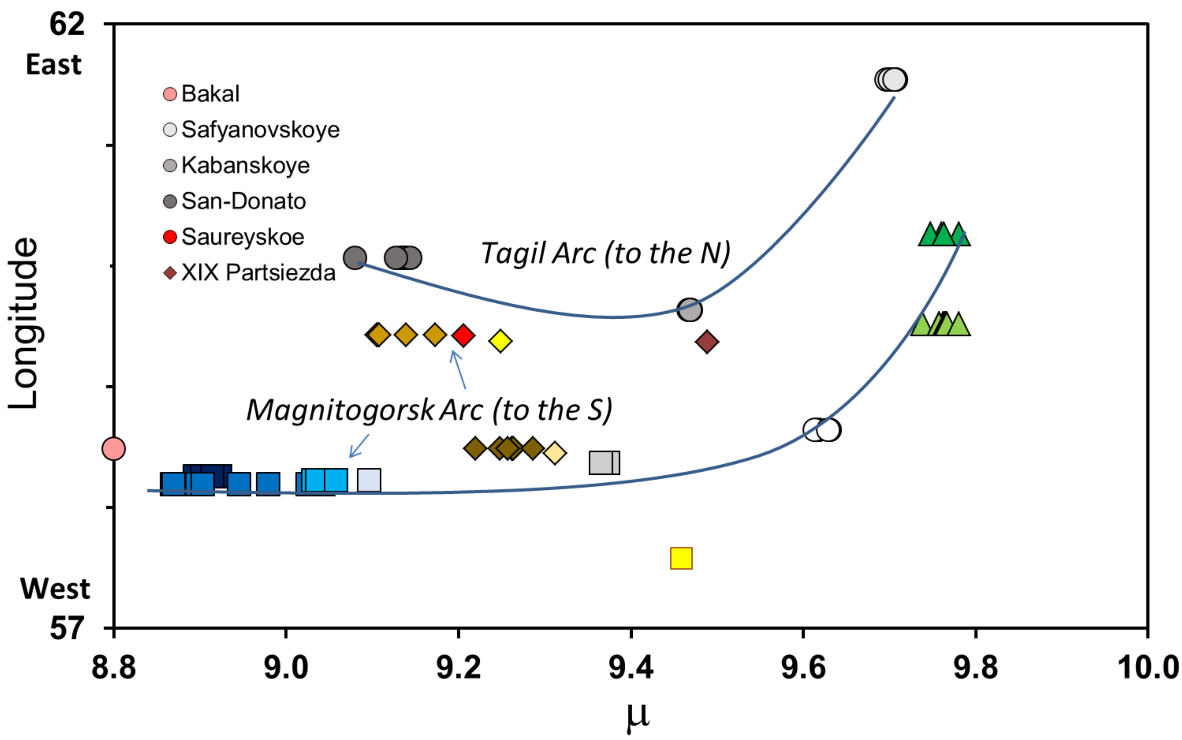


A
B
2.7 Ga
Age = 2701±150 Ma
15.6
15.4
15.2
15.0
14.8
14.6
13.5
14.5
15.5
16.5
17.5
18.5
207Pb/204Pb
206Pb/204Pb



B
IPB
Intra-arc
Back-arc
Orogene
Proterozoic
crust / sediments
Urals VHMS
Ordovician
crust / sediments
Growth curve
Arc
Ordovician
MORB - Urals
Fore-arc
Archaean
crust
NHRL
Fore-Arc zone
Island Arc zone
Back-Arc and rifted arc zones
Sakmara Allochton
15.6
15.5
15.4
17.2
17.4
17.6
17.8
18
18.2
18.4
$^{207}Pb/^{204}Pb$
$^{206}Pb/^{204}Pb$

Fig. 7.



62
East
West
57
Longitude
Bakal
Safyanovskoye
Kabanskoye
San-Donato
Saureyskoe
XIX Partsiezda
Tagil Arc (to the N)
Magnitogorsk Arc (to the S)
8.8
9.0
9.2
9.4
9.6
9.8
10.0
μ

Fig. 8.

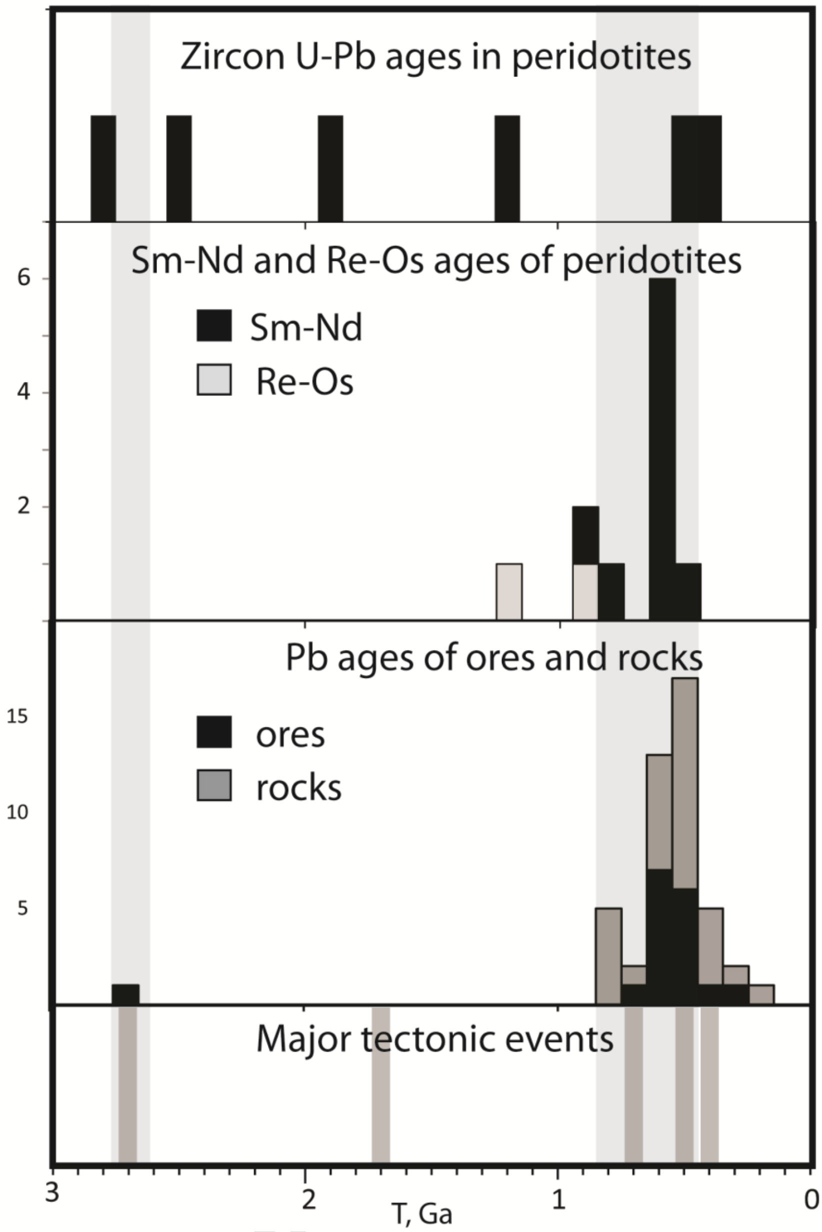
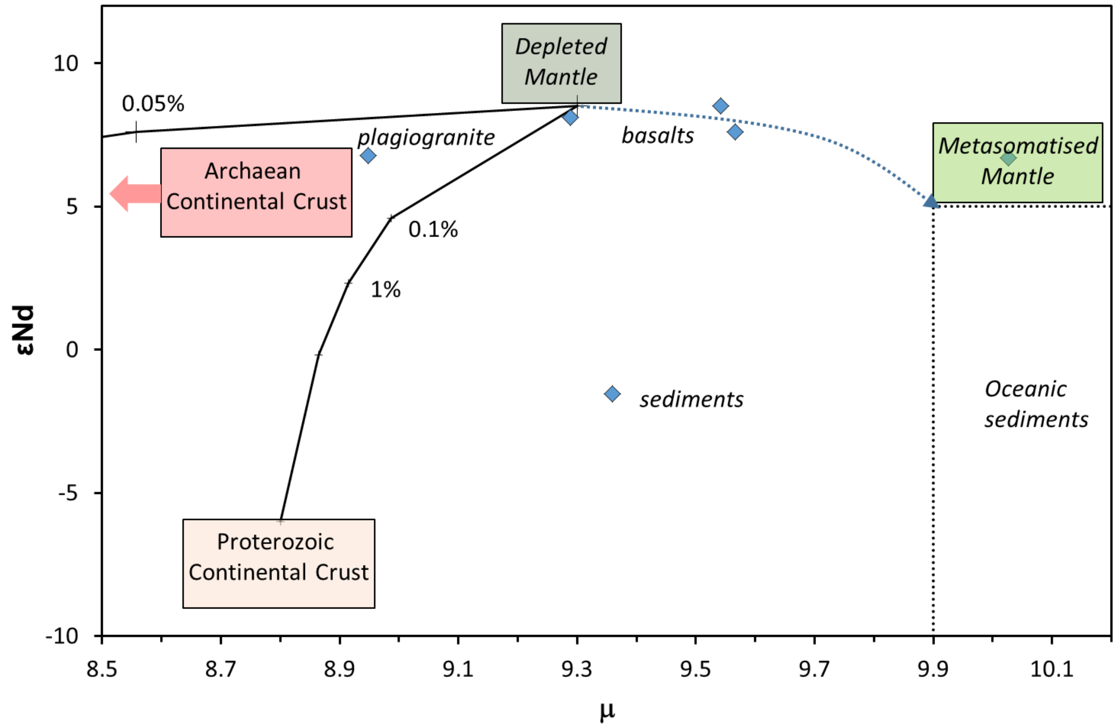
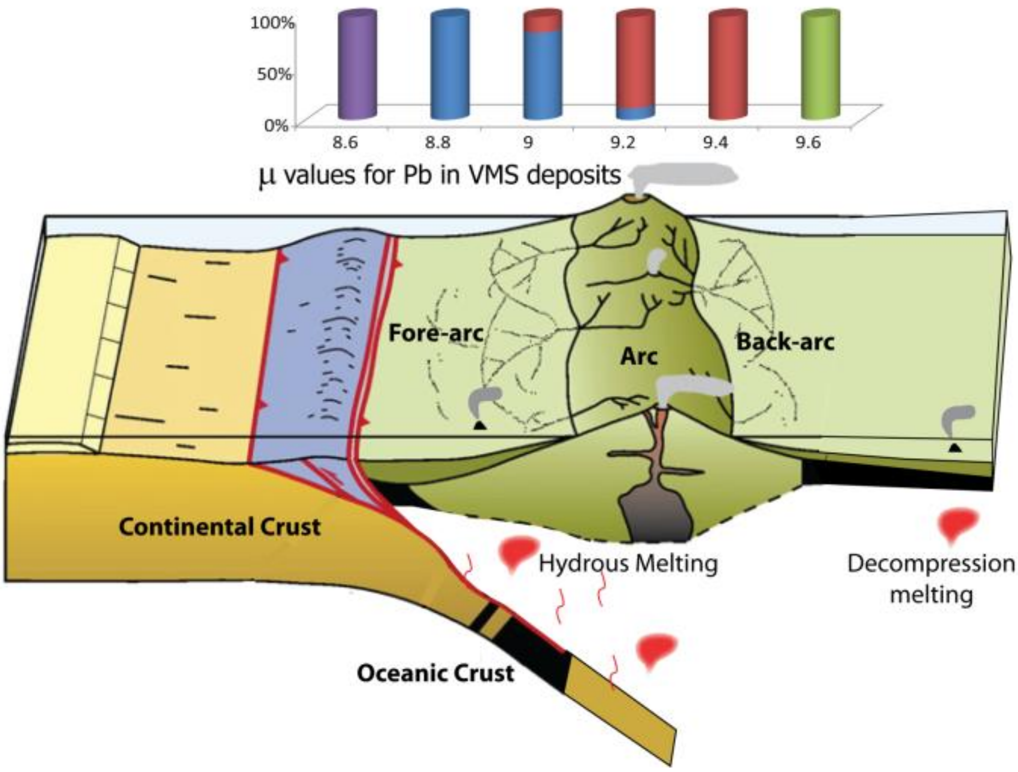

Zircon U-Pb ages in peridotites
Sm-Nd and Re-Os ages of peridotites
Sm-Nd
Re-Os
6
4
2
Pb ages of ores and rocks
ores
rocks
15
10
5
Major tectonic events
3
2
1
0
T, Ga

Figure 9.



10
5
0
-5
-10
εNd
8.5
8.7
8.9
9.1
9.3
9.5
9.7
9.9
10.1
μ
Depleted Mantle
0.05%
plagiogranite
basalts
Metasomatised Mantle
Archaean Continental Crust
0.1%
1%
sediments
Oceanic sediments
Proterozoic Continental Crust

Fig. 10.



100%
50%
0%
8.6
8.8
9
9.2
9.4
9.6
μ values for Pb in VMS deposits
Fore-arc
Arc
Back-arc
Continental Crust
Hydrous Melting
Decompression melting
Oceanic Crust

Fig. 11.

Table 1. Lead isotopic composition of galenas from sulphide ores in the Urals. The high-precision data analysed using a Tl-spike are shown by (*). T = model age (Stacey & Kramers, 1975), $\mu = ^{238}U/^{204}Pb$.

Deposit	Type of ore	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	T, Ma	μ
Fore-arc zone						
Oktiabrskoye (3)	Massive ores	17.474	15.478	37.214	628	8.88
	Massive ores*	17.481	15.486	37.256	639	8.89
Bakr-Tau (4)	Massive ores	17.467	15.511	37.292	696	8.87
	Massive ores	17.437	15.484	37.201	668	8.83
	Gal-Chp-Shp ores	17.442	15.486	37.210	668	8.84
	Massive ores	17.618	15.539	37.518	637	9.09
	Massive ores	17.649	15.528	37.517	594	9.13
	Gal-Sph ores*	17.574	15.509	37.381	614	9.03
Uvariag (6)	Massive ores	17.579	15.494	37.329	579	9.03
Balta-Tau (5)	Massive ores*	17.818	15.532	37.611	472	9.37
	Massive ores*	17.822	15.542	37.618	486	9.37
	Massive ores*	17.816	15.528	37.603	464	9.37
Tash-Tau (6)	Massive ores	17.625	15.510	37.408	574	9.10
Arc (*West-Magnitogorsk zone*)						
Gai (7)	Massive ores	17.712	15.504	37.452	496	9.22
Podolskoye (8)	Massive ores	17.778	15.524	37.554	485	9.31
Sibai (9)	Stockwork*	18.005	15.569	37.827	405	9.63
	Massive ores*	17.996	15.569	37.824	412	9.62
	Massive ores*	17.993	15.570	37.832	415	9.61
Molodezhnoye (10)	Gal-Sph massive ores	17.714	15.554	37.590	595	9.22
	Massive ores	17.691	15.529	37.542	562	9.19
Uchaly (11)	Stockwork	17.641	15.545	37.512	632	9.12
	Massive Py ores*	17.632	15.549	37.509	646	9.11
	Gal vein in the dyke*	17.631	15.550	37.507	647	9.11
	Gal-Sph massive ores*	17.655	15.554	37.521	639	9.14
	Massive Chp ores*	17.633	15.548	37.508	643	9.11
	Later nodule from the upper part	18.197	15.580	37.972	266	9.90
Babarik (12)	Massive ores*	17.695	15.533	37.532	568	9.20
Alexandrinskoye (12)	Stockwork*	17.733	15.531	37.559	534	9.25
	Massive ores	17.746	15.543	37.599	548	9.27
	Massive ores	17.746	15.542	37.597	546	9.27
	Massive ores	17.746	15.537	37.571	536	9.27
	Massive ores	17.746	15.528	37.538	518	9.27
	Massive ores	17.751	15.551	37.622	561	9.27
	Massive ores on flank	17.751	15.548	37.616	554	9.27
	Massive ores	17.753	15.545	37.598	546	9.28
	Massive ores	17.767	15.558	37.658	562	9.30
	Massive ores	17.741	15.534	37.564	534	9.26
	Massive ores	17.743	15.535	37.566	534	9.26
	Massive ores	17.732	15.521	37.524	514	9.25
	Massive ores	17.741	15.535	37.564	536	9.26
	Massive ores	17.743	15.540	37.580	544	9.26
	Massive ores	17.735	15.528	37.539	526	9.25
	Massive ores	17.729	15.525	37.533	525	9.24
	Massive ores	17.726	15.515	37.503	507	9.24
	Massive ores	17.731	15.526	37.533	525	9.25
	Duplicate	17.724	15.513	37.498	505	9.24
	Gal vein in the dyke	17.730	15.520	37.515	514	9.24
	Stockwork zone	17.732	15.523	37.530	519	9.25
	Gal-Ba ores	17.706	15.520	37.502	531	9.21
	Cerusite from subcont. alt. zone	17.746	15.546	37.601	554	9.27
	Later barite-Q vein	18.087	15.529	37.544	257	9.75

Back-arc zone						
Dzhusa (13)	Massive ores	18.081	15.589	37.892	388	9.74
	Massive ores	18.095	15.609	37.955	416	9.76
Barsuchii Log (14)	Chp-Py fine clastic ores	18.097	15.610	37.969	417	9.76
	Massive ores	18.111	15.630	38.027	444	9.78
	Massive ores	18.088	15.603	37.938	410	9.75
Sakmara zone (allochton ?)						
Yaman-Kasy (2)	Massive ores*	17.883	15.547	37.666	451	9.46
	Massive ores	17.882	15.518	37.573	394	9.46
Bashkirian anticlinorium (Proterozoic sediments)						
Bakal (1)	Massive ores	17.414	15.580	37.218	864	8.80
Polar Urals (Ordovician platform)						
Saureyskoe (17)	Massive ores	18.251	15.593	37.999	266	9.98
	Massive ores	18.262	15.605	38.041	282	9.99
	Massive ores	18.259	15.603	38.029	280	9.99

Table 2. U-Pb elemental and Pb isotopic composition of massive sulphide ores and volcanic and sedimentary host rocks in the Urals, corrected for U decay over 400 Ma. Mineral abbreviations: Py-pyrite; Mc – marcasite; Chp-chalcopyrite; Po – pyrrhotite.

Sample ID	*Location*	*Lithology*	*Pb*	*U*	*Atomic ratio*	*Initial ratio 400 Ma*	T, Ma

			(ppm)	(ppm)	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	
Sakmara zone										
00YKL 08	Yaman-Kasy	basalt			18.430	15.576	38.132	17.875	15.545	454
Main Uralian Fault Suture zone (ores)										
D 62.5	Dergamish	Py-Mc	11.20	0.83	18.461	15.574		18.125	15.556	284
Iv 148.2	Ivanov-skoye	Chp-Py	1.38	0.001	18.008	15.584		18.004	15.584	434
Iv 80.5		Py-Po diss.	5.87	0.004	18.014	15.582		18.010	15.582	425
Iv 126.5		coarse Po	0.60	0.001	17.996	15.612		17.989	15.612	500
IS 0108	Ishkinino	Py-Chp	1.59	0.077	17.994	15.569		17.774	15.557	553
rocks										
D 41.0	Dergamish	serpentinite	0.51	0.014	23.855	15.823	38.014	23.731	15.816	
D 46.3		pillow breccia	2.3	5.79	17.782	15.542	37.578	6.357	14.917	
Der 011		basalte	2.87	0.32	18.281	15.568	37.859	17.775	15.540	519
DER 012			1.76	0.77	19.504	15.643	37.973	17.519	15.534	701
DER 013		serpentinite	0.25	0.58	18.020	15.562	37.705	7.491	14.986	
Iv 33.6	Ivanov-skoye	serpentinite			18.286	15.597	38.064	18.286	15.597	247
Iv 136.0		gabbro	3.93	0.14	18.137	15.569	37.873	17.975	15.560	409
Iv 011		basalt	0.32	0.36	19.633	15.633	38.883	14.528	15.354	
Iv 012			1	0.48	18.477	15.579	38.061	16.299	15.460	
Isk 012			1.36	0.15	18.321	15.551	38.023	17.820	15.524	452
Isk 014		sediments	4.94	0.15	18.040	15.553	37.854	17.903	15.545	433
West-Magnitogorsk zone										
00 KT 16	Irendik		0.83	0.47	19.956	15.647	38.806	17.387	15.506	750
00 PG 07	Bogachev M.	plagiogranite	1.12	0.53	19.760	15.604	38.618	17.613	15.487	538
00 PG 11		plagiogranite	3.93	0.85	18.227	15.537	37.842	17.246	15.483	815
Inter-arc bassin										
00 SY 12	Karam. Sibay	basalt	2.28	0.08	18.118	15.562	37.835	17.959	15.554	408
00 KM 02	Karam. Mnt	andesite	1.23	0.57	19.467	15.642	37.950	17.364	15.527	806
East-Magnitogorsk zone										
5915/524	Alexandrinskoye	dacite	2.79	0.81	18.745	15.599	38.535	17.427	15.527	758
859/108.0		dacite	2.45	0.78	18.817	15.587	38.686	17.372	15.508	763
5983/111		dacite metas.	60.6	0.97	17.798	15.531	37.576	17.725	15.527	531
6025/241.3		dacite metas.	42.9	1.04	17.830	15.533	37.597	17.720	15.526	535
5999/157.8		dacite	4.03	1.25	18.748	15.593	38.471	17.341	15.516	804
AD4		gabbro dyke	8.36	0.23	17.834	15.529	37.609	17.709	15.522	534
5902/497		basalte	4792	0.14	17.761	15.562	37.651	17.761	15.562	575
5913/163		andesite	19	1.01	17.958	15.537	37.745	17.717	15.523	531
5969/59		gossan	212	4.02	17.782	15.542	37.578	17.696	15.537	575
5906/475		pelitolite	15.8	0.4	17.913	15.540	37.724	17.798	15.534	490
5900/582		pelitolite	10.2	0.2	17.900	15.554	37.782	17.811	15.549	510
6025/168.3		sediments	2366	8.08	17.769	15.563	37.647	17.753	15.562	580
6096/208.5		plagiogranite	5.9	1.13	18.388	15.554	37.892	17.519	15.506	648
R 5002	Rossipniansy M	plagiogranite	4.24	0.78	18.443	15.582	38.120	17.609	15.537	639

Note: abbreviation metas. means metasomatised

Table 3. Sm-Nd elemental and Nd-Os isotopic composition of selected volcanic rocks and sediments from Urals. See Table 2 for samples description.

	Sm (ppm)	**Nd (ppm)**	**$^{147}Sm/^{144}Nd$**	**$^{143}Nd/^{144}Nd$**	ε_{Nd}
Iv33.6	0.29	0.90	0.1988	0.512990	6.76
SY12	0.90	2.53	0.2187	0.513086	7.61
859/108	1.18	3.72	0.1959	0.512958	6.29
5902/497	1.78	6.45	0.1702	0.512985	8.12
5900/582	1.87	9.13	0.1263	0.512375	-1.53

5969/59	2.56	8.29	0.1904	0.512821	3.89
6096/208.5	2.28	8.90	0.1582	0.512884	6.77
PG 11	2.24	11.28	0.1225	0.512739	5.77

Table 4. Summary of lead isotopic compositions for studied VHMS deposits along with model ages and calculated μ values (μ reflects the average U/Pb ratio in the lead source). These are shown according to geodynamic setting within an island arc structure. The lead isotopic composition of the Proterozoic Bakal deposit from an adjacent continent is shown for comparison.

Tectonic setting	VHMS deposits	Rocks series	Biostrati-graphic age, Ma	Model age Ma (2-stage model)	Source μ	Possible source of lead
Bashkirian anticlinorium	Bakal	Proterozoic carbonate-rich sediments		897	8.8	Continental
Fore-arc	Bakr-Tau, Oktiabrskoye, Tash-Tau, Balta-Tau, Uvariag	Boninitic at the bottom, calc-alcaline (Baymak-Buribay F)	400-395	484-696	8.8-9.2	Continental (Bash. Anticlin.)
Arc	Podolskoe, Gay, Alexandrinskoye, Molodezhnoye, Uchaly	Toleiitic (Karamalitash), & Calc-alcaline rocks	392-388	505 – 630	9.0–9.4	Mixed: Arc volcanics & Continental
Rifted Arc	Sibai	Toleiitic (Karamalitash)	380	410	9.6	Arc volcanics
Back-arc	Barsuchii Log, Dzhusa	Unknown (Upper Baymak-Buribay?)		390 - 445	~9.6	Arc volcanics
Sakmara Allochton	Yaman-Kasy		420 (?)	423	9.5	Arc volcanics

Table 5. The end-members compositions for mixing model including μ and ε(400)Nd components.

End-member	μ	Pb, ppm	ε(400)Nd	Nd, ppm	References
Archaean Continental Crust	4.1*	20	-17	44	Bibikova et al 2009
Proterozoic Continental Crust	8.8	20	-6*	44	This work
Depleted Mantle	9.3	0.06	8.5	0.6	Spadea and d'Antonio, 2006
Metasomatised Mantle	10		6.7		This work
Oceanic sediments	9.9-11.6		5 – (-10)		Ben Othman (1989); Plank and Langmuir (1998)

Note. * data not available; parameter was calculated according to model growth curves.

No conflict of interest is present

Highlights to the paper:

"Lead isotopic systematics of massive sulphide deposits in the Urals: applications for geodynamic setting and metal sources" by Tessalina et al.

- Lead isotopic data from Southern Urals VHMS deposits display a systematic increase in lead isotopic ratios across the Magnitogorsk paleo-island arc zone, with the fore-arc having the least radiogenic lead compositions and the back-arc having the most radiogenic lead. The back arc lead model ages are close to the biostratigraphic ages of the ore-hosting volcano-sedimentary rocks (*ca*. 400 Ma). In contrast, less radiogenic lead from the fore-arc gives Neoproterozoic (~700 Ma) to Cambrian (480 Ma) lead model ages with low two-stage model μ ($^{238}U/^{204}Pb$) values of 8.8, progressively increasing stratigraphically upwards to 9.4 in the cross-section of the ore-hosting Baimak-Buribai suite.
- The most radiogenic lead found in VHMS deposits and volcanics from the Main Uralian Fault suture zone, rifted-arc and back-arc settings, and show similar isotopic composition with the Urals Ordovician MORBs. Radiogenic composition of Urals MORB ($\Delta\ ^{207}Pb/^{204}Pb$ = 11) and related deposits is explained by derivation of lead from highly depleted mantle metasomatized during dehydrational partial melting of subducted slab and oceanic sediments.
- The range of age-corrected uranogenic lead isotopic ratios of the volcanic and sedimentary host rocks is also quite large: $^{206}Pb/^{204}Pb$ =17.25-17.96; $^{207}Pb/^{204}Pb$ = 15.48-15.56, and generally matches the ores, with the exception of felsic volcanics and plagiogranite from the Karamalytash Formation being less radiogenic compare to the basaltic part of the cross-section, which would potentially imply a different source for the generation of felsic volcanics.
- The unradiogenic source of lead may be represented by Neoproterozic oceanic crust, evidenced by multiple Neoproterzoic ages of mafic-ultramafic massifs across the Urals. The relics of these massifs were attributed by some workers to the earlier Neoproterozoic stage of pre-Uralian ocean development. Alternative sources of lead may be constituted by old Archean continental crust fragments/sediments sourced from the adjacent East-European continent, or Proterozoic sediments accumulated near the adjacent continent and presently outcropping near the western edge of Urals (Bashkirian anticlinorium). The contribution of Archean rocks/sediments to the Urals volcanic rock formation is estimated to be less than 0.1% based on Pb-Nd mixing model.