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### **Biostratigraphy versus isotope geochronology: Testing the Urals island arc model**

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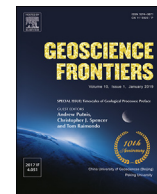


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## Research Paper

# Biostratigraphy versus isotope geochronology: Testing the Urals island arc model

Svetlana Tessalina<sup>a,b,\*</sup>, Cristina Talavera<sup>a,b,c</sup>, Michael E. Pritchinn<sup>d</sup>, Victor Puchkov<sup>d,e</sup><sup>a</sup>John de Laeter Centre for Isotope Research, Curtin University, GPO Box U 1987, Kent St, Bentley, WA 6102, Australia<sup>b</sup>The Institute for Geoscience Research (TIGeR), Curtin University, GPO Box U 1987, Kent St, Bentley, WA 6102, Australia<sup>c</sup>School of GeoSciences, The King's Buildings, James Hutton Road, Edinburgh EH9 3FE, United Kingdom<sup>d</sup>Institute of Geology and Geochemistry, Urals Branch of Russian Academy of Sciences, 15 Akademika Vonsovskogo Str., Ekaterinburg, 620016, Russia<sup>e</sup>Institute of Geology, Ufimian Scientific Investigation Centre, K.Marx st. 16/2, 450077, Ufa, Russia

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## ABSTRACT

Formation of the Urals volcanic-hosted massive sulphide (VHMS) deposits is considered to be related with the intra-oceanic stage of island arc(s) development in the Upper Ordovician–Middle Devonian based on the biostratigraphic record of ore-hosting sedimentary rocks. However, the direct Re-Os dating of four known VHMS systems in the Urals gives significantly younger Re-Os isochron ages ranging from  $355 \pm 15$  Ma up to  $366 \pm 2$  Ma. To address this discrepancy, we performed SHRIMP U-Pb dating on zircons extracted from rhyodacites (Eifelian biostratigraphic age of 393–388 Ma) from the footwall of the Alexandrinka VHMS deposit which has a Re-Os isochron age of sulphides of  $355 \pm 15$  Ma.

New  $^{206}\text{Pb}/^{238}\text{U}$  mean age of  $374 \pm 3$  Ma (MSWD = 1.4 and probability = 0.11) is considered to be the crystallisation age of the host volcanic rock. This age is ca. 15 Ma younger than the Eifelian (393–388 Ma) biostratigraphic age and overlaps the Frasnian–Famennian boundary ( $372 \pm 2$  Ma), characterised by the final stages of Magnitogorsk Arc – East European continent collision. Such an inconsistency with geochronological age may be due to a reburial of conodonts during resedimentation as a result of erosion of older rocks in younger sedimentary sequences.

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## 1. Introduction

The age of the Urals VHMS deposits is currently thought to be Upper Ordovician to Middle Devonian and formed in an intra-oceanic arc setting (e.g., Prokin and Buslaev, 1999; Herrington et al., 2005). These deposits are considered to be synchronous to the formation of ore-bearing volcano-sedimentary rocks which have been dated using biostratigraphic methods (e.g., Artyuszkova and Maslov, 2008; Puchkov, 2010; Puchkov, 2017). There are few radiometric ages of ore hosting volcanics and where available they appear to be discordant with known biostratigraphic ages (Ronkin et al., 2016). Moreover, the direct Re-Os dating of four known Urals VHMS systems using ore sulphides (mainly pyrite) for the Dergamish, Alexandrinka and Yaman-Ksy deposits and molybdenite

for the Kul-Yurt-Tau deposit, gives significantly younger Re-Os isochron ages ranging from  $355 \pm 15$  Ma up to  $366 \pm 2$  Ma (Gannoun et al., 2003; Tessalina et al., 2008, 2017). To address this age discrepancy, we dated by SHRIMP zircons separated from rhyodacites which have an Eifelian (393–388 Ma) biostratigraphic age based on conodonts. These rocks are situated in the footwall of the Alexandrinka VHMS deposit, which has a Re-Os isochron age of sulphides of  $355 \pm 15$  Ma (Tessalina et al., 2008).

## 2. Geological setting and sampling

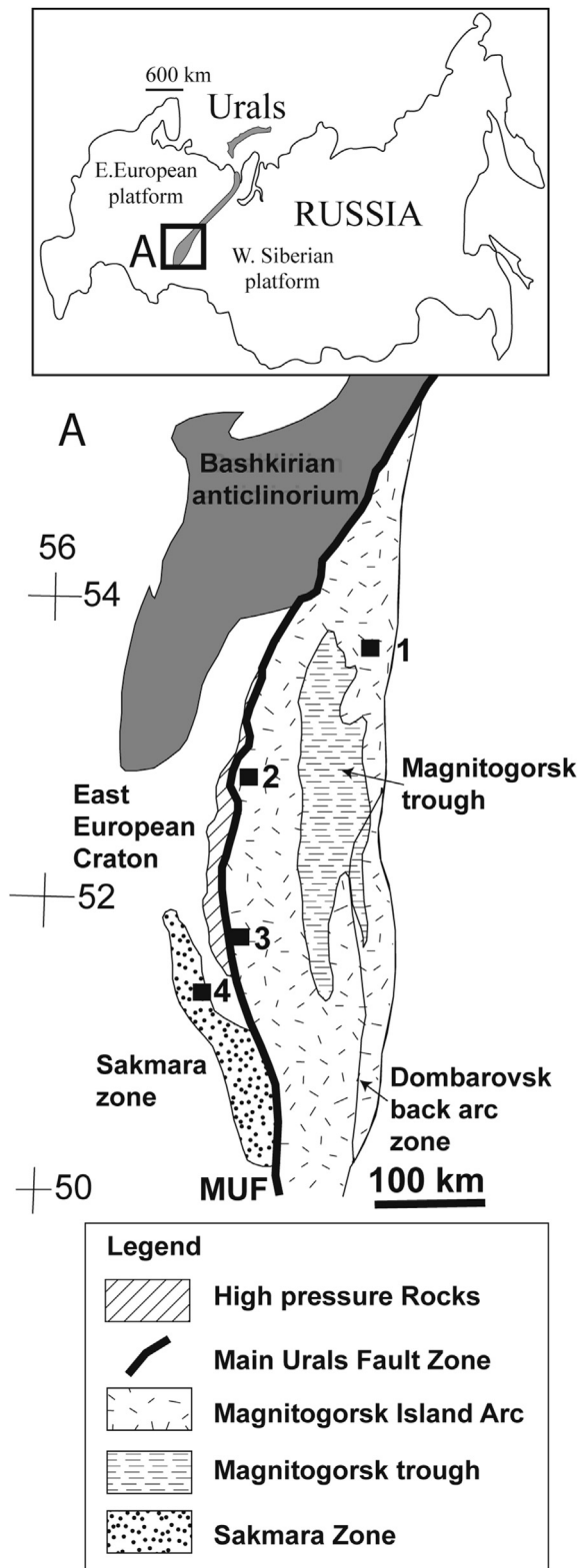
### 2.1. Urals

The Urals are considered to be one of the world's largest provinces of VHMS deposits, second only to the Iberian Pyrite Belt VHMS province (Spain-Portugal) in term of ore reserves. It is an orogenic belt 2000 km in length, which marks the geographic boundary between Europe and Asia (Fig. 1). The Urals consists of a composite of intra-oceanic island arc terranes amalgamated

\* Corresponding author. John de Laeter Centre for Isotope Research, Curtin University, GPO Box U 1987, Kent St, Bentley, WA 6102, Australia.

E-mail address: [Svetlana.Tessalina@curtin.edu.au](mailto:Svetlana.Tessalina@curtin.edu.au) (S. Tessalina).

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**Figure 1.** Simplified geological map of the Southern Urals showing the main regions of arc volcanic sequences and the location of studied Alexandrinka VHMS deposit, as well as other deposits mentioned in the text. The following subdivisions are shown: (1) Main Urals 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 volcanics and sediments of Devonian age. An intermediate “intra-arc” basin, filled by Late Devonian–Lower Carboniferous volcanics and sediments, divides the Magnitogorsk structure into the West and East-Magnitogorsk zones; (3) Sakmara allochthon, whose origin is not clear. Massive sulphide deposits: 1 – Alexandrinka, 2 – Kul-Yurt-Tau, 3 – Dergamish, 4 – Yaman-Kasy.

Thickness (m)	ALEXANDRINKA deposit	
	Lithology	Description
	• • • • •	flysch sediments
0-200	[Lithology symbols: horizontal lines, wavy lines]	limestone
0 - 2	[Lithology symbols: wavy lines]	ore level
30-200	[Lithology symbols: triangles, circles]	felsic rocks
0-40	[Lithology symbols: triangles, circles]	basalt
10-50	[Lithology symbols: triangles, circles, filled square]	ore-bearing volcanoclastic felsic rocks
200-250	[Lithology symbols: triangles, circles]	andesite-dacite-rhyolite
	[Lithology symbols: triangles, circles]	basalt

**Figure 2.** Stratigraphic column of the Alexandrinka deposit showing location of rhyodacite sample (filled square within the section of ‘ore-bearing volcanoclastic felsic rocks’).

together between the East European continent and Kazakhstan microcontinent (e.g., Herrington et al., 2005; Puchkov, 2010).

The Magnitogorsk arc is host to the number of the Urals VHMS deposits and contains preserved early forearc assemblage, arc tholeiite to calc-alkaline sequences and rifted arc bimodal tholeiitic sequences (e.g., Herrington et al., 2005). The boninitic rocks of the forearc host Cu-Co VHMS deposits, situated within the Main Urals Fault suture zone, which is marking the line of arc-continental collision started in Upper Devonian times. The arc tholeiites host Cu-Zn deposits, with an evolution to more calc-alkaline felsic volcanic sequences matched with a change to Zn-Pb-Cu polymetallic deposits. Large rifts in the arc sequence are filled by thick bimodal tholeiite sequences, showing evolution towards more calc-alkaline nature. These thick bimodal sequences are host to the largest of the Cu-Zn ‘Uralian’-type deposits (Herrington et al., 2005).

According to tectonic reconstructions by Herrington and Brown (2011), Puchkov (2010) among others, the formation of the Urals VHMS deposits spanned ca. 75 Ma, from Upper Ordovician to Middle Devonian (458–383 Ma), and was separated into several metallogenic epochs. The oldest one is related with the Ordovician Guberlyta arc (Dubinina and Ryazantsev, 2008; Puchkov, 2017), hosting several VHMS deposits in the Sakmara zone (including Yaman-Kasy; Fig. 1). The next stage of the VHMS deposits formation is related with the Tagil arc, which occurs in the Northern part of the Urals and is not considered in this study (see Prokin and Buslaev, 1999; for more details). The latest Late Emsian–Middle Devonian (405–383 Ma) epoch is linked to the Magnitogorsk arc

and hosts several VHMS deposits including Alexandrinka (see Fig. 1).

No VHMS deposit formation was reported in rocks deposited in the period from the end of the Eifelian (ca. 388 Ma), whereas the intense island-arc volcanism was still active in the territory of the East-Magnitogorsk Zone. The beginning of collision caused the accumulation of the Zilair Formation in the West-Magnitogorsk zone, with volcano-clastic sediments supply from persistent volcanism in the East-Magnitogorsk Zone.

The geological history and chronostratigraphy of the Devonian mineralisation and related sedimentation in the Southern Urals was characterised in detail using the conodont scale (Artyushkova and Maslov, 2008; Maslov and Artyushkova, 2010), giving constraints on the age of volcanics and associated VHMS deposits, and is briefly outlined below.

During the *serotinus* Zone (Emsian, Lower Devonian; 408–393 Ma), relatively vigorous volcanism begins in the submarine extensional structures (rifts). Rhyolite-basaltic volcanogenic sequences of this age (Baimak-Buribai and Kiembai formations in the Magnitogorsk Megazone) formed and host numerous polymetallic deposits of Kuroko type (e.g., Balta-Tau, Kul-Yurt-Tau, Barsuchi Log).

A significant deepening of the basin was associated with rhyolite-basaltic volcanism in extensional settings (rifts) at the end of the *costatus* Conodont Zone and continued through the *australis* and *kockelianus* zones (Eifelian, Middle Devonian: 393–388 Ma), giving rise to the Karamalytash and Alexandrinka Formation, which hosts a great number of large and giant VHMS deposits of Uralian type within the Magnitogorsk zone (e.g., Uchali, Sibai, Alexandrinka).

No VHMS deposit formation is reported in rocks deposited in the period from the end of the Givetian to the early Frasnian (ca. 383 Ma), whereas the intense island-arc volcanism was still active on the territory of the East-Magnitogorsk Zone. The longest time span without any volcanic activity falls within the *punctata* – *rhenana* zones (Frasnian, Upper Devonian: 383–372 Ma), when the relatively shallow-water regime abruptly changed to a deep-water one. After a long dormant volcanic period and sedimentation the next extensive outbreak in volcanic activity falls within the Frasnian/Famennian boundary interval (ca. 372 Ma). The

beginning of collision caused the accumulation of the Zilair flysch Formation in the West-Magnitogorsk zone, with volcano-clastic sediments supply from persistent volcanism in the East-Magnitogorsk Zone.

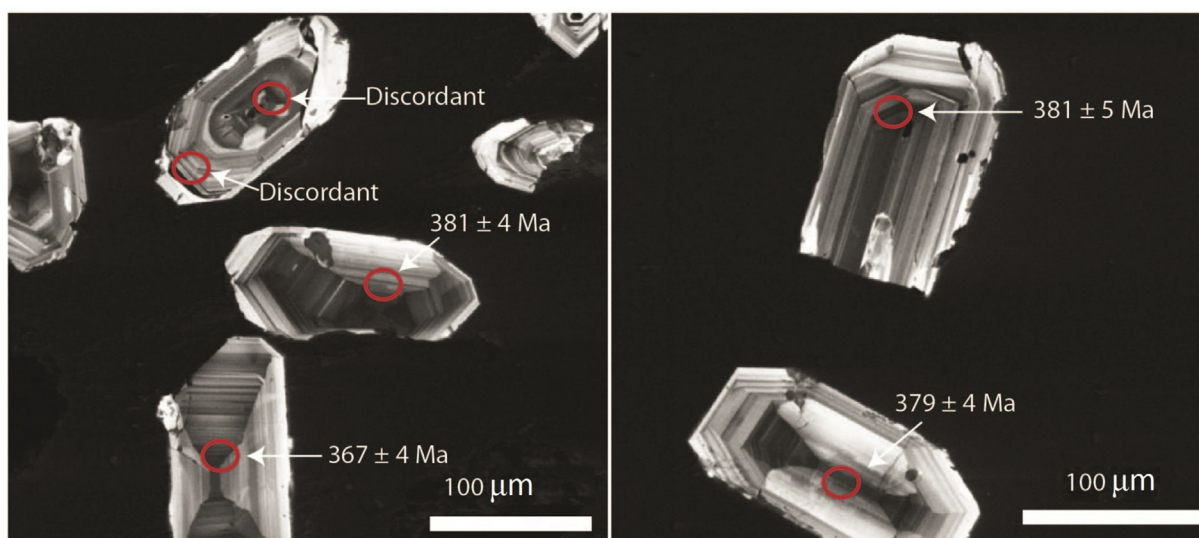
## 2.2. Alexandrinka deposit

The Alexandrinka deposit (e.g., Tessalina et al., 2008) is located at 53°31'N and 59°22'E and is 25 km northeast of the city of Magnitogorsk within the Middle Devonian East-Magnitogorsk island arc zone (Fig. 1).

The Alexandrinka deposit is situated within a NE trending linear depression filled by volcano-sedimentary rocks and flanked by a chain of rhyolitic domes and a ridge of basalt (Fig. 2). The trough contains 23 orebodies located on the NE slope of this depression. The deposit is hosted by the Eifelian (ca. 393–388 Ma) Alexandrinka Formation, in which three units are recognised: (1) a pre-ore basaltic unit, >1000 m thick, (2) an ore-bearing rhyodacite with small phenocrysts, 200–300 m thick, and (3) a supra-ore basalt–rhyolite unit with silicic volcanics rich in large phenocrysts, 100–200 m thick (Fig. 2). A representative sample from unit 2 was collected from the open pit for zircon geochronology. The Alexandrinka Formation is overlain by limestone, hornblende–plagioclase andesite, dacite and flyschoid terrigenous clastic rocks. Late diabase dikes and a subvolcanic dacite sill are located to the southeast of the deposit. The main orebody is localised at the contact between the overlying basalt and the underlying acid volcanics within the volcano-sedimentary member.

Host volcano-sedimentary rocks consist of disintegrated aphyric and porphyritic dacites with small phenocrysts and of volcanoclastic rocks (xenolith-bearing lavas) containing fragments of basalt, rhyolite, dacite, silicified volcanics, jasper, chloritite, sulfide ore, and some intrusive rocks. Rare interlayers of pink and greenish grey argillites, dolostone, chloritite, sulfide siltstone, sandstone, and quartz–carbonate–hematite rock, formed by submarine oxidation of sulfide ore (gossans), are also present.

Herrington et al. (2002) noted the distinctly calc-alkaline nature of the volcanic rocks hosting Alexandrinka deposit, which differ them from more tholeiitic rocks of the neighbouring Karamalytash Formation.



**Figure 3.** Catholuminescence (CL) images of zircons from the rhyodacite sample (footwall of Alexandrinka deposit). Red spot is area of SHRIMP analysis. Ages and errors are from Table 1.

**Table 1**

U–Pb data for zircons from rhyolite sample in the footwall of the Alexandrinka massive sulphide deposit (see Fig. 2 for sample location in stratigraphic sequence).

Analysis	U (ppm)	Th (ppm)	$^{232}\text{Th}/^{238}\text{U}$	$\%^{206}\text{Pb}^c$	$^{204}\text{Pb}/^{206}\text{Pb}$	$\pm\%$	$^{207}\text{Pb}^*/^{206}\text{Pb}^*$	$\pm\%$	$^{207}\text{Pb}^*/^{235}\text{U}$	$\pm\%$	$^{206}\text{Pb}^*/^{238}\text{U}$	$\pm\%$	err corr	$^{207}\text{Pb}_{\text{corr}}/^{206}\text{Pb}/^{238}\text{U}$ age (Ma)	% Discordant
ALEXz1	181	57	0.327	0.23	1.40E-04	58	0.0538	2.8	0.435	3.1	0.0586	1.2	0.4	367 ± 4	-1
ALEXz2	299	141	0.488	0.05	2.70E-05	100	0.0542	1.6	0.456	1.9	0.061	1.1	0.6	381 ± 4	0
ALEXz3	152	56	0.379	0.32	2.10E-04	50	0.0535	3.5	0.441	3.7	0.0598	1.2	0.3	374 ± 5	-6
ALEXz4	197	89	0.469	0.2	4.60E-05	100	0.0548	3.2	0.442	3.4	0.0585	1.2	0.3	366 ± 4	9
ALEXz6	65	23	0.362	-	-2.70E-04	71	0.0562	5.7	0.462	5.9	0.0597	1.5	0.3	373 ± 5	19
ALEXz7	148	57	0.398	0.77	3.80E-04	38	0.0546	4.4	0.444	4.7	0.0591	1.6	0.3	370 ± 6	6
ALEXz8	174	62	0.37	0.68	9.90E-04	21	0.045	7.4	0.373	7.5	0.0601	1.3	0.2	380 ± 4	801
ALEXz9	104	37	0.364	0.07	7.60E-05	100	0.0535	3.1	0.44	3.7	0.0596	2	0.5	374 ± 7	-6
ALEXz10	128	46	0.372	0.15	3.70E-04	41	0.0497	5.1	0.405	5.2	0.0591	1.3	0.2	372 ± 5	-106
ALEXz11	395	216	0.566	0.14	1.70E-04	35	0.0529	2.1	0.442	2.3	0.0606	1.1	0.5	380 ± 4	-17
ALEXz12	288	129	0.462	0.65	3.00E-04	32	0.0551	2.9	0.465	3.5	0.0613	1.9	0.5	383 ± 7	8
ALEXz13	56	14	0.255	0.01	-3.10E-04	71	0.0586	6.3	0.477	6.5	0.059	1.6	0.2	368 ± 6	34
ALEXz14	61	14	0.241	0.32	-	-	0.0568	3.2	0.475	3.5	0.0607	1.5	0.4	379 ± 6	22
ALEXz15	153	62	0.42	0.62	5.50E-04	32	0.0509	5.5	0.413	5.8	0.0589	1.6	0.3	370 ± 6	-58
ALEXz16	239	93	0.402	0.04	7.60E-05	71	0.0534	2.2	0.446	2.5	0.0605	1.2	0.5	379 ± 4	-10
ALEXz17	412	301	0.754	0.13	-2.10E-05	100	0.0556	1.3	0.468	1.9	0.061	1.4	0.7	381 ± 5	13
ALEXz18	185	69	0.384	0.72	7.90E-04	24	0.0479	7.1	0.377	7.2	0.0571	1.2	0.2	361 ± 4	-281
ALEXz19	217	110	0.524	0.32	7.80E-05	71	0.0554	2.2	0.453	2.9	0.0593	1.9	0.7	371 ± 7	14
ALEXz20	189	69	0.375	0.28	9.00E-05	71	0.0549	2.5	0.442	2.7	0.0584	1.2	0.4	366 ± 4	10
ALEXz5c	346	270	0.808	8.38	4.20E-03	15	0.0611	19.6	0.526	19.7	0.0625	1.9	0.1	388 ± 6	40
ALEXz5r	267	104	0.404	55.27	3.10E-02	2	0.0439	61	0.319	61.1	0.0528	3.3	0.1	335 ± 6	389

• $\%^{206}\text{Pb}^c$  is % of  $^{206}\text{Pb}$  from common Pb.•Errors are  $1\sigma$ .

•Pb\* indicates radiogenic Pb, corrected for common Pb.

Analysis references: ALEXz is zircon from rhyodacite collected in the footwall of the Alexandrinka deposit, followed by grain number ± “c” or “r”, meaning core or rim, respectively.

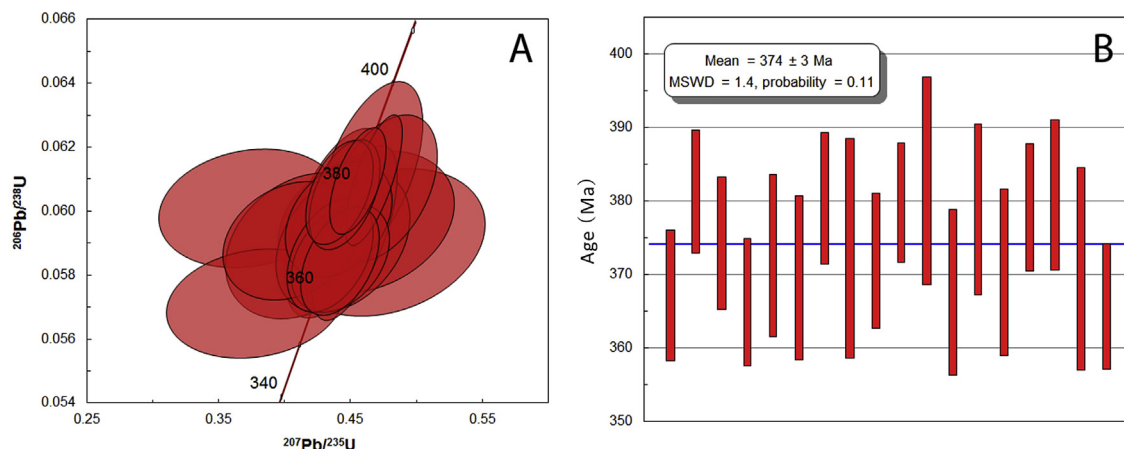
### 3. Method

Numerous zircons grains were extracted using conventional heavy liquid and magnetic separation. Approximately seventy zircon grains were handpicked from the zircon concentrate and mounted in an epoxy disc together with zircon standards. The mounted zircons were imaged by cathodoluminescence imaging on a Mira3 FESEM instrument in the John de Laeter Centre (JdLC). Representative CL images are shown on Fig. 3 for some of the analysed grains.

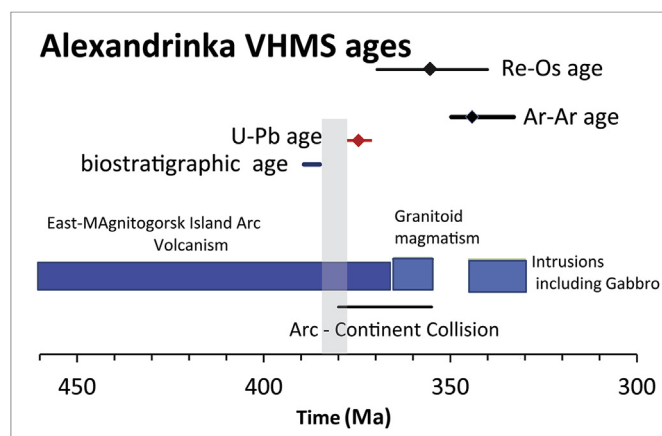
Analyses were undertaken on a SHRIMP II instrument at the John de Laeter Centre for Isotope Research at Curtin University. The analytical procedures for the Curtin consortium SHRIMP II have been described by De Laeter and Kennedy (1998), and Kennedy and de Laeter (1994) and are similar to those described by Compston et al. (1984) and Williams (1998). A 20–25  $\mu\text{m}$  diameter spot is used, with a mass-filtered  $\text{O}_2$ -primary beam of  $\sim 2.1$ – $2.3$  nA on zircons. Data for each spot is collected in sets of 6 scans on the

zircons through the mass range of  $^{196}\text{Zr}_2\text{O}^+$ ,  $^{204}\text{Pb}^+$ , Background,  $^{206}\text{Pb}^+$ ,  $^{207}\text{Pb}^+$ ,  $^{208}\text{Pb}^+$ ,  $^{238}\text{U}^+$ ,  $^{248}\text{ThO}^+$  and  $^{254}\text{UO}^+$ . The  $^{206}\text{Pb}/^{238}\text{U}$  age standard and U-content standard used is BR266 (559 Ma and 903 ppm U; Stern, 2001). The  $^{207}\text{Pb}/^{206}\text{Pb}$  standard used to monitor instrument induced mass fractionation is OGC zircon (3467 ± 3 Ma; Stern et al., 2009). The  $^{207}\text{Pb}/^{206}\text{Pb}$  dates obtained on OGC zircons during the SHRIMP sessions matched the  $^{207}\text{Pb}/^{206}\text{Pb}$  standard age within uncertainty and no fractionated correction was warranted. The common Pb correction was done using the “207-correction” which is calculated by projecting the uncorrected analyses onto concordia from the assumed common  $^{207}\text{Pb}/^{206}\text{Pb}$  present-day composition and from the measured  $^{204}\text{Pb}$  using the  $^{204}\text{Pb}/^{207}\text{Pb}$  ratios provided by the Stacey and Kramers (1975) model at the calculated age. The programs SQUID II and Isoplot (Ludwig, 2003, 2009) were used for data processing.

Errors cited for individual analysis include errors from counting statistics and the common-Pb corrections are at the  $1\sigma$  level. The U-



**Figure 4.** (A) Data for zircons studied on a Wetherill Concordia Diagram. Ellipses show  $2\sigma$  uncertainties. (B) Selected  $^{207}\text{Pb}$ -corrected  $^{206}\text{Pb}/^{238}\text{U}$  age data ( $n = 18$ ) for zircons.



**Figure 5.** Time line of Alexandrinka deposit formation using different radiogenic isotope systematics (Re-Os: Tessalina et al., 2008; Ar-Ar: Tessalina et al., 2017; U-Pb – this work) in a framework of East-Magnitogorsk island arc development (Puchkov, 2010). Note that the difference between biostratigraphy and U-Pb ages places Alexandrinka deposit in a different geodynamic context (Arc-Continent collision).

Pb calibration error based on reproducibility of U-Pb measurements of the standard was added on the pooled age. Dates for which the  $^{206}\text{Pb}$  of common Pb was  $>1\%$  were not considered in the age discussion or plotted on the Wetherill Concordia diagrams. However, they are listed on Table 1. Weighted mean values for ages given on pooled analyses are at the 95% confidence level. Uncertainty ellipses shown in the figures are at the  $2\sigma$  uncertainties, unless otherwise stated. Ages in the text and figure are quoted as  $^{206}\text{Pb}/^{238}\text{U}$  dates.

#### 4. Results

Zircons from the rhyodacite are pale pink to colourless. Under the scanning electron microscope, these zircons are subhedral to euhedral, bipyramidal prisms, and show continuous oscillatory zoning typical of igneous zircons (Fig. 3). No inherited cores were found. Twenty grains selected from both core and rim zones were analysed on the SHRIMP. Nineteen of twenty analyses yielded concordant dates ranging from 361 Ma to 383 Ma (Fig. 4 and Table 1). Eighteen analyses plot in a single population with a  $^{207}\text{Pb}$ -corrected  $^{206}\text{Pb}/^{238}\text{U}$  mean age of  $374 \pm 3$  Ma (MSWD = 1.4 and probability = 0.11) (Fig. 4). There is one younger date at 361 Ma which has been omitted in the calculation of the age as a statistical outlier. The Th/U ratios of these grains range from 0.24 to 0.75, which is typical of magmatic zircons, with U and Th contents of 61–412 ppm and 14–301 ppm, respectively (Table 1). The internal growth structure of the zircons shows typical igneous, continuous, oscillatory zoning and do not display any partial dissolution and reprecipitation textures of pre-existing zircons which might indicate a post-crystallisation event. Therefore, the Th/U ratios together with the internal and external morphology of these zircons suggest that the ca. 374 Ma age represents the crystallisation age of this volcanic rock.

#### 5. Discussion – application for Urals VHMS deposits geodynamic setting

##### 5.1. Significance of new U-Pb zircon age

The U-Pb age of the zircons from the rhyodacite underlying the Alexandrinka orebody ( $374 \pm 3$  Ma; this study) is nearly within the error of the Re-Os age of the sulphide ores from the same deposit ( $355 \pm 15$  Ma; Tessalina et al., 2008), and about 15 Ma younger than biostratigraphic Middle Devonian Eifelian age (ca. 393–388 Ma)

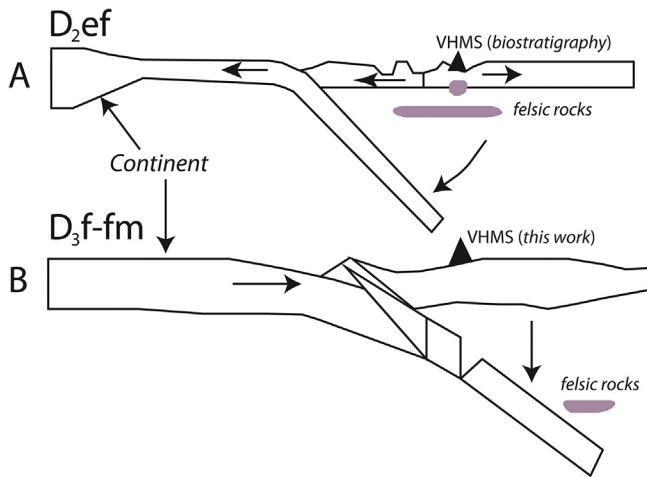
based on conodonts record described by Maslov and Artyuszkova (2010) (Fig. 5). The anomalously young rhyodacite U/Pb age presented herein requires re-examination of existing conodont-based biostratigraphy. In general, conodonts are recognised as a reliable stratigraphic tool. Such an inconsistency of conodont-based biostratigraphy with geochronological age is quite rare and mostly related to a resedimentation due to erosion of older rocks and reburial of conodonts in younger sedimentary sequences. Therefore until now we have no indications of such event from the conodont workers of the region.

According to currently accepted model, the Southern Urals volcanogenic massive sulphide deposits have been formed in intra-oceanic arc setting and spans a period of time from ca. 460 Ma to 385 Ma (e.g., Artyuszkova and Maslov, 2008; Puchkov, 2010; Herrington and Brown, 2011) (Fig. 6). In the Southern Urals, the initiation of intra-oceanic subduction during the Lower Devonian (ca. 400 Ma) triggered the volcanism leading to the Magnitogorsk island arc development. By the Upper Devonian, the young volcanic arc began to collide with the margin of the adjacent Laurussia continent. The timing of this collision event was established at 380–355 Ma, based on  $^{40}\text{Ar}/^{39}\text{Ar}$ , U-Pb and Sm-Nd dating of high-pressure metamorphic rocks and sediments belonging to the continental margin (Beane and Connelly, 2000; Puchkov, 2010). Our new zircon age ( $374 \pm 3$  Ma) corresponds to the final stages of this collision event, being close within the error to the Frasnian–Famennian boundary ( $372.2 \pm 1.6$  Ma; International Chronostratigraphic Chart, 2017/2).

The entrance of cooler and less dense continental crust into the subduction zone caused the cessation of magmatic activity for  $\sim 10$  Ma (375–365 Ma; Fershtater et al., 2007) and decreased the angle of subduction slab, which in turn initiated the generation of shallow volatile-rich felsic magmas. A number of Middle to Late Devonian Cu(Au)-porphyry deposits have been linked to gabbrodiorite and felsic intrusions generated under these conditions (e.g. Voznesenskoe, Alapaevsk-Sukhoy Log cluster, Yubileynoe; see Plotinskaya et al., 2017). For example, plagiogranite porphyry rocks related to the Yubileynoe Cu-Au-porphyry deposit have been dated at  $374 \pm 3$  Ma (Grabezhev, 2014). The source of primary melts for those rocks was ascribed to the mantle wedge with variable contamination by older continental material from the slab (Grabezhev, 2014), expressed by negative Nd signatures (ca.  $\epsilon_{\text{Nd}}$  of 2; Grabezhev, 2014).

In the case of the Alexandrinka deposit, one can expect the contribution from the older continental rocks of the slab to be seen in the sources of primary melts and/or metals. Uranium-corrected lead isotopic compositions of felsic rocks (dacites) display unradiogenic values with model ages ranging from 760 Ma to 800 Ma, decreasing up to ca. 530 Ma for metasomatised rocks (Tessalina et al., 2016). The  $\epsilon_{\text{Nd}}$  values, however, remain in the ‘depleted mantle’ field ranging from +6.3 for the felsic rocks up to +8.1 in basalts from the Alexandrinka deposit. Moreover, lead isotopic compositions of Alexandrinka ores display an “old” unradiogenic signature with Neoproterozoic to Cambrian model ages (505–562 Ma), similar to metasomatic felsic rocks, and  $\mu$  (parameter  $\mu = ^{238}\text{U}/^{204}\text{Pb}$  reflects the averaged U/Pb ratio in the lead source) values of 9.2–9.3 are intermediate between regional “depleted mantle” and “continental crust” material (see Tessalina et al., 2016, for details). This Pb isotopic composition is difficult to explain in a framework of the intra-oceanic subduction model (Tessalina et al., 2016). In the Southern Urals, the Pb isotope data suggest progressive increase in  $\mu$  values (interpreted as contribution of fluids from the subducted continental crust/sediments) across the subduction front, becoming almost nil in some of the mature arc and back-arc settings.

On more global scale, the closure of Uralian paleo-ocean corresponds to the amalgamation of Laurussia, Siberia and China-Korea



**Figure 6.** Geodynamic models for: (A) Eifelian time (biostratigraphic age for the Alexandrinka Formation) and (B) Frasnian-Famennian time (U-Pb age of rhyodacite in our work). Geodynamic setting corresponds to (A) mature arc and (B) collisional stages of Magnitogorsk island arc development. Figure is reproduced after Puchkov (2010).

paleocontinents. The fundamental plate boundary rearrangements in the Late Devonian appears to be marked by intense magmatism under tectonic activation, manifested in island arc volcanism paired with episodic continental rifting, as well as hydrothermal activity on rifted or faulted outer continental margins, comprising large cluster of VHMS deposits in Spain and Portugal (Iberian Pyrite Belt province), Rudny Altai (Siberia), and the North American margin (Alaska) (e.g., Dusel-Bacon et al., 2004; Tornos et al., 2005; Chiaradia et al., 2006). These deposits are formed in local extensional volcanic basins within an overall contractional geodynamic environment during or after termination of convergence by accretion of an island arc or crustal block (Huston et al., 2010), and are characterised by metal contributions from the continental crust.

The largest Iberian Pyrite Belt province was formed as a result of extension induced by oblique collision of tectonic blocks (Tornos et al., 2005), represented by an island arc and continental blocks (Gondwana and Laurentia plates) in the Late Devonian (ca. 355 Ma), about 10 Ma after the beginning of High-Pressure eclogite-facies metamorphism (365–370 Ma; Rodriguez et al., 2003).

The Devonian Rudny Altai Province (Siberia) is a host of several VHMS deposits. This terrain is a part of the Altaid orogen which formed by aggregation of Paleozoic subduction–accretion complexes and Precambrian basement blocks (e.g., Chiaradia et al., 2006).

The Zn–Pb–Ag mineralization along the ancient Pacific margin of North America (Alaska) was formed in the Late Devonian (ca. 370 Ma; Dusel-Bacon et al., 2004) in a within-plate (extensional) tectonic setting resulted from attenuation of the ancient continental margin of western North America, or as a result of development of an arc (Dusel-Bacon et al., 2004 and references therein).

Thus, the Urals represent only one example of large Devonian metallogenic province interpreted to be entirely formed within the intra-oceanic arc setting. This fact is rather ambiguous given that the modern deposits in intra-oceanic arcs tend to be small and form at low temperatures (Hannington et al., 2005). Further geochronological-field studies are needed to elucidate the place of VHMS deposits in the Urals history.

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