Abrupt and moderate climate changes in the mid-latitudes of Asia during the Holocene

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ABSTRACT. A multiple parameter dating technique was used to establish a depth/age scale for a 171.3 m (145.87 m w.e.) surface to bedrock ice core (Bl2003) recovered from the cold recrystallization accumulation zone of the Western Belukha Plateau (4115 m a.s.l.) in the Siberian Altai Mountains. The ice-core record presented visible layering of annual accumulation and of $\delta^{18}O/\delta D$ stable isotopes, and a clear tritium reference horizon. A steady-state glacier flow model for layer thinning was calibrated and applied to establish a depth/age scale. Four radiocarbon (14C) measurements of particulate organic carbon contained in ice-core samples revealed dates for the bottom part of Bl2003 from 9075 ± 1221 cal a BC at 145.2 ± 0.1 m w.e. (0.665 m w.e. from the bedrock) to 790 ± 93 AD at 121.1 m w.e. depth. Sulfate peaks coincident with volcanic eruptions, the Tunguska meteorite event, and the 1842 dust storm were used to verify dating. Analysis of the Bl2003 ice core reveals that the modern Altai glaciers were formed during the Younger Dryas (YD) (~10950 to ~7500 cal a BC), and that they survived the Holocene Climate Optimum (HCO) (~6500 to ~3600 cal a BC) and the Medieval Warm Period (MWP) (~640 to ~1100 AD). A decrease in air temperature at the beginning and an abrupt increase at the end of the YD were identified. Intensification of winds and dust loading related to Asian desert expansion also characterized the YD. During the YD major ion concentrations increased significantly, up to 50 times for Na $^+$ (background), up to 45 times for Ca $^{2+}$ and Mg $^{2+}$, and up to 20 times for SO $_4^{2-}$ relative to the recent warm period from 1993 to 2003. A warm period lasted for about three centuries following the YD signaling onset of the HCO. A significant and prolonged decrease in air temperature from ~2000 to ~600 cal a BC was associated with a severe centennial drought (SCD). A sharp increase in air temperatures after the SCD was coincident with the MWP. After the MWP a cooling was followed gradually with further onset of the Little Ice Age. During the modern warm period (1973-2003) an increase in air temperature is noted, which nearly reaches the average of HCO and MWP air temperature values.

KEYWORDS: ice-core records, isotope chemistry, paleoclimatic reconstruction

1. INTRODUCTION

The climatic system exhibits moderate, abrupt and threshold state changes over a wide range of time. This range in variability is explored through the analysis of past climate in order to predict future climate. The retreat or advance of alpine glaciers at low-, mid- and high latitudes of Asia is one of the most obvious and significant consequences of climate variability (Haeberli and Holzhauser, 2003; Li and others, 2006; Narama and others, 2006). Over the past 150 years, since the end of the Little Ice Age (LIA), alpine glaciers all over the world have tended to retreat (Mayewski and

Jeschke, 1979; Kadota and others, 1997; Paul and others, 2004; Liu and others, 2006; Aizen, 2011) in response to rapid increase of air temperature coupled with changes in precipitation patterns in mountain regions.

The rate of the glacier area change between the 1950s and 2010s varied from -5% for large glacier massifs in the central Pamir and central Tien Shan to -28% for small cirque and piedmont glaciers in the Siberian Altai, western and eastern Tien Shan (Surazakov and Aizen, 2006; Aizen and others, 2007; Aizen, 2011; IPCC, 2014).

Existing ensembles of climate models predict further largescale warming in central Asia (IPCC, 2014), although details of regional climate predictions for high mountain regions and

† Deceased

particularly for central Asia remain unclear (e.g. Mitchell and others, 2004; UNEP, 2008). Instrumental climate records barely cover the past 100 years in Asian mountains and the data are sparse. There is still scientific uncertainty about the age of present glaciations, for example whether they existed after the Last Glacial Maximum (LGM) during the Bølling–Allerød (BA) or instead developed after the interstadial BA during the Younger Dryas (YD) (Grosswald, 1980; Velichko and others, 1984, 2002; Velichko and Isayeva, 1992; Grosswald and others, 1994; Shatravin, 2000; Kuhle, 2004).

Long ice-core records from polar and alpine regions provide one of the most robust historical archives of the Earth's climate, allowing evaluation of the moderate, abrupt, and even threshold climatic conditions (O'Brien and others, 1995; Mayewski and others, 2004, 2005; IPICS, 2005). In temperate latitudes, long ice-core records can preserve records of accumulated climatic conditions extending back several millennia (Thompson and others, 1997, 2003). The goal of this research is to estimate the dynamics of moderate, and abrupt climatic changes in alpine glaciations in the mid-latitudes of Asia based on a surface to bedrock ice core from the Siberian Altai.

The Siberian Altai glacier system encompasses the continental northern periphery of the Central Asian Mountain System and the southern periphery of the Asian Arctic basin (Fig. 1) and is therefore a geographically ideal area to develop climatic records relating to major Eurasian circulation systems as well as internal and external hydrological cycles over northern Eurasia (Aizen and others, 2005). Paleo-climatic records recovered from Altai ice cores provide data that are complementary to records already developed from other Asian cores (e.g. Sentik, Dunde, Dasuopu, Guliya, Xixipangma and Everest) (e.g. Thompson and others, 1989, 2000; Kang and others, 2000; Qin and others, 2006; Tian and others, 2006). In contrast to the Tibetan/Himalayan ice-core records that have been recovered from monsoon-dominated circulation regions, the Altai Mountains act as the initial barrier in central Asia to intrusion of cold air masses from the Arctic. There have been no surface to bedrock ice-core records recovered from the Asian sector of the Arctic to compare to existing Arctic/ Greenland ice cores (e.g. Mayewski and others, 1993, 1994, 2004; Alley and others, 1997). Altai glacier records are directly associated with water vapor advected from the Atlantic and Pacific oceans and from the large Aral-Caspian internal drainage water system to the Arctic Ocean through Siberian rivers (Aizen and others, 2005).

2. DATA AND METHODS

2.1. Field research

The research presented here is the result of joint USA/Japan/ Russia glaciological expeditions to the Siberian Altai in 2001, 2002 and 2003 (Fujita and others, 2004; Aizen and others, 2005, 2006; Nakazawa and others, 2005; Okamoto and others, 2011). The Western Belukha Plateau at the northern edge of the central Asian mountain system was selected as the most suitable site for ice-core drilling. The plateau is ~1 km² and maintains an accumulation area of cold, recrystallized snow/firn (Aizen and others, 2005). The surface velocity at the drilling site is <0.45 m a⁻¹. Maximum ice thickness, determined by radio-echo sounding measurements, is 180 m. Two ice cores were drilled in 2003 on the

plateau (Bl2003; 49°48′N, 86°33′E, 4115 m a.s.l.) (Fig. 1), westward from West Belukha Peak (4435 m a.s.l.): one core was drilled to a depth of 171.3 m (surface to bedrock), and the second was drilled to a depth of 47.8 m from the surface.

An electro-mechanical drill with an inner diameter of 9.5 cm and a 135 cm long barrel (Geo-Tech Co., Japan), was used for drilling. With the 171.3 m borehole, the drill cutters touched bedrock. Our radar measurements of the ice thickness and bedrock topography showed that West Belukha Plateau lies on a relatively smooth flat bedrock, composed of plagiogranite and granodiorites (Berzin and Kungurtsev, 1996).

Ice-core densities and preliminary stratigraphic descriptions of ice layers and grain sizes were documented in the field via photographic and written records (Takeuchi and others, 2004). The core from the surface to ~40 m depth consisted of a mixture of compacted firn and bubbly ice with thin transparent ice layers related to summers (Fig. 2a). The transparent layers of ice in the ice-core sections are gradually merged into a single mass of ice below 60 m of depth based on visual inspection.

Temperature was measured every 10 m in the 171 m deep borehole (Takeuchi and others, 2004; Aizen and others, 2006) (Fig. 2b). From 0 °C at the snow surface, temperature dropped to -10 °C at 2 m, to -15.8 °C at 50–70 m depth and to -14.4 °C at the bottom, i.e. lower than the annual mean air temperature (-12.9 °C for the period 1973–2003; Aizen and others, 2005) at this elevation. The ice temperature suggests that West Belukha Plateau lies in the cold recrystallization zone, where any meltwater subsequently refreezes below the surface. Since the -14.4 °C ice temperature at the bedrock is below the eutectic temperature, there should be no ion diffusion in the Bl2003 ice core (lizuka and others, 2012).

Bulk density of the cores increased with depth, and reached 930 kg m⁻³ at ~60 m w.e. (Fig. 2c). A density/depth profile was constructed allowing the w.e. thickness to be determined. All depths from this point in the paper are presented as w.e. depths. The ice-core length is 145.87 m w.e. Using insulated boxes, the ice cores were transported frozen to the ice-core laboratory at the Research Institute for Humanity and Nature (RIHN) in Japan. There, core sections were halved lengthwise and shipped frozen to the Ice Core Laboratory at the University of Idaho (UI).

2.2. Ice-core processing and geochemical analysis

Ice-core physical stratigraphy was conducted in the UI Ice Core Laboratory, the National Ice Core Laboratory, USA and the RIHN. After detailed stratigraphic documentation, the inner part of ice from each section (4 cm × 4 cm) was cut and shipped frozen to the Climate Change Institute (CCI) at the University of Maine (UM). At the CCI dedicated ice-core laboratory, ice-core sections were melted in a modified 'Wagenbach-style' continuous melter system connected with multiple fraction collectors to melt the core sections into discrete, co-registered samples at 0.01–0.08 m w.e. resolution (Fig. 3a, 4252 samples). The samples were immediately refrozen to await geochemical analysis. Osterberg and others (2006) provide full details of the melter system accuracy, precision and detection limits. Major ion analysis was performed via suppressed ion chromatography using a

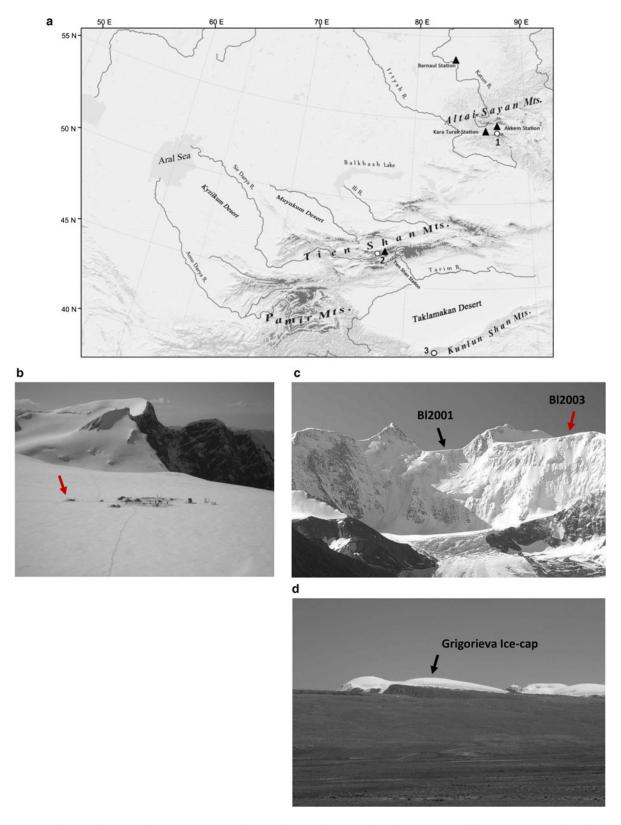


Fig. 1. (a) Map of central Asia with ice-coring sites (white circles) and meteorological stations used for ice-core records calibration and validation (black triangles). (b) Western Belukha Plateau, ice-coring site (BL2003, number 1 on the map), 4115 m a.s.l., August 2003, Siberian Altai. (c) Location of two drilling sites at the Belukha Mt massif: Bl2001 – between the east and west Belukha Peaks at 4062 m a. s.l. (Olivier and others, 2003) and Bl2003. (d) Grigor'eva ice cap in Tien Shan, (Gr2007, No. 2 on the map) at 4563 m a.s.l. (Takeuchi and others, 2014). No. 3 on the map is the ice core from the Guliya ice cap in Tibet (Thompson and others, 1997).

Dionex DX500 system at the ppb level with minimum detectable concentrations of 1 ppb.

Stable isotope ratios (δ^{18} O, δ D) were determined via headspace equilibration at the UI Stable Isotope Laboratory using a Finnigan Delta Plus isotope ratio mass spectrometer coupled with Finnigan's GasBench II.

Oxygen isotope ratios were measured using a standard CO_2 equilibration technique (Craig, 1957) with a Micromass multi-prep device coupled to a SIRA mass spectrometer. Hydrogen isotope ratios were measured using Cr reduction with a Eurovector elemental analyzer coupled to a Micromass Isoprime mass spectrometer (Morrison and

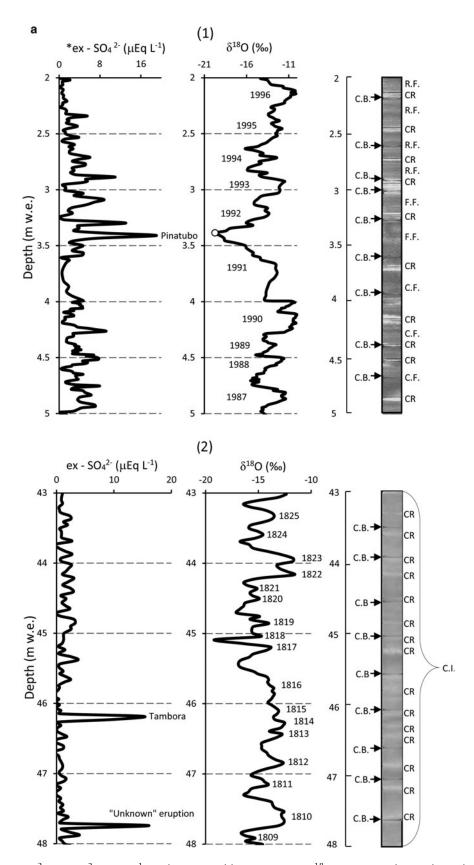


Fig. 2. Profiles of (a) *ex-SO₄²⁻, ex- SO₄²⁻ (μEq L⁻¹), and oxygen stable isotope ratios δ^{18} O (‰) seasonal-annual signals from two parts of icecore sections: from 1987 to 1997, e.g. from 5 to 2 m w.e. (1) and from 1809 to1826, e.g. from 48 to 43 m w.e. (2) of Bl2003 ice-core, and corresponding visual stratigraphy composed of a mosaic of digital pictures of ice-core sections: C.B signifies a break between the core sections; R.F. is regelated coarse-grained firm with few 1–2 mm ice crusts; F.F. is fine-grained firm with multiply 2–3 mm radiative ice crusts; C.F. is compact medium-grained snow/firn; C.I. is compact ice; CR is transparent ice interlayers identified compacted summer ice crusts. (b) The borehole temperature and (c) ice-core density (surface to the bedrock ice-core) (Takeuchi and others, 2004).

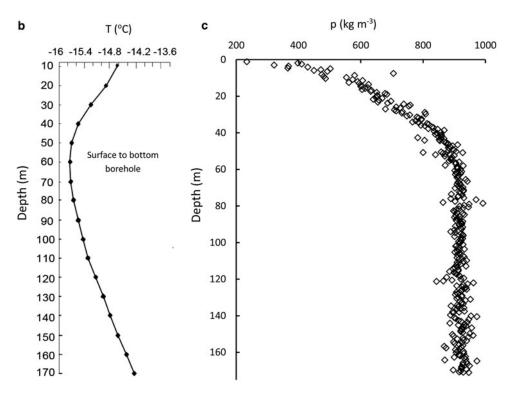


Fig. 2. (continued).

others, 2001). Data are reported in standard delta (δ) notation vs Standard Mean Ocean Water. The analytical precision for measurements of oxygen and deuterium isotope ratios was ± 0.05 and $\pm 0.5\%$, respectively. Analytic uncertainty in d-ex was 0.5%, calculated from the quadratic average of the uncertainty for δ D and $8 \times \delta^{18}$ O (Froehlich and others, 2002). Stable isotope ratios (δ^{18} O, δ D) determined at UI were validated with corresponding isotope data from Nagoya University (NU), Japan (Fig. 3b). UI stable isotope samples were analyzed at 0.01–0.08 m w.e. resolution (Fig. 3a) for the 145.87 m w.e. surface to the bedrock core, while NU stable isotope samples were analyzed at 0.10 m resolution to a depth of 68.7 m w.e. (87.4 m) for the same surface to bedrock core. The NU stable

isotope samples (1594 samples) were interpolated for validating the UI data.

2.3. Tritium measurements

Tritium concentrations (³H) were measured via liquid scintillation counting at National Institute for Polar Research (NIPR, Japan) by analyzing 178 samples at a resolution of 0.06–0.59 m and verified in the Idaho State University, Environmental Monitoring Laboratory USA (ISU) by analyzing seven non coregistered samples within 1 m above and below the depth of maximum concentration determined at NIPR. Average difference between the four ISU samples and the NIPR results was <13TU, i.e. <2% of the maximum concentration.

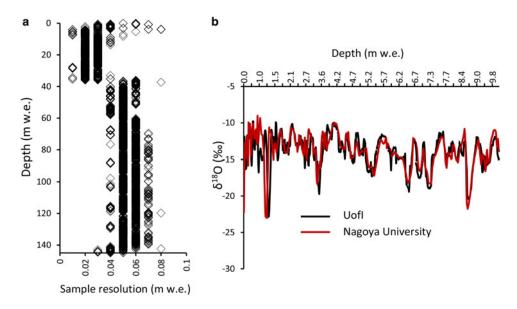


Fig. 3. The profiles of (a) sample length in the Bl2003 ice core and (b) oxygen stable isotope ratios, δ^{18} O (‰). The results received in Uofl and validated with corresponding isotope data at Nagoya University.

2.4. ¹⁴C radiocarbon measurements

Radiocarbon analysis of the particulate organic carbon (POC) fraction was conducted at the Laboratory of Radio and Environmental Chemistry, Paul Scherrer Institute according to the method described by Jenk and others (2006) and Sigl and others (2009). Prior to analysis ice-core segments were cut in the cold room to obtain sections of clear ice. Ice layers with visible high dust loading or coarse lithoidal particles were not used for dating to avoid potential age interferences of old mineral carbon with the organic carbon fraction. Ice samples were thoroughly decontaminated by removing outer layers in a three-step process (cutting with a band saw, scraping with a scalpel, rinsing with 18 $M\Omega$ cm ultrapure water) to eliminate potential contamination from sampling and handling operations. Melted samples were then filtered through quartz fiber filters (Pallflex Tissuquartz, 2500QAO-UP; prebaked) and carbonates were removed by acidification of the filter residue with 0.2 M HCl. Dried filters were combusted in a two-step process where the fractions of POC and elemental carbon are separated (10 min at 340 °C, 12 min at 650 °C) followed by cryogenic trapping and manometric quantification of the evolving CO₂ (Szidat and others, 2004). The CO₂ samples were sealed in glass ampoules, which were fixed to the gas handling system of the 200 kV accelerator mass spectrometer system MICADAS for 14C determination at the ETH Laboratory of Ion Beam Physics (Ruff and others, 2007; Synal and others, 2007). Results were corrected for a blank input of $1.5 \pm 0.7 \,\mu\text{gC}$ with a fraction of modern $f_{\rm m} = 0.64$ ±0.11. For calibration OxCal 4.1 (Bronk, 2001) and the IntCal09 data of Reimer and others (2009) were used.

2.5. Meteorological data

Data from meteorological stations (daily, event, monthly and annual) for the period 1950-2002 were used for climatic analysis. The Akkem station (49°54′N, 86°32′E; 2045 m) has over 50 years of instrumental record, is in close proximity to the drill site (within 10 km), sits at a relatively high elevation compared with other nearby stations, and is positioned to record the main air masses moving from the west toward the drill site (Fig. 1a) (Aizen and others, 2005). Barnaul station (53°17'N, 83°39 E; 185 m) data were also used because that station has the longest (1838 to present) instrumental record in the region. It is located 450 km northwest of the drill site. An AWS installed near the drill site recorded the main meteorological parameters every 3 h during 2002/03 and resulting data are highly correlated with the Akkem station data. Akkem station and West Belukha Plateau temperature data for the period, July 2002 to April 2003 are also correlated, with $R^2 = 0.87$ (Okamoto and others, 2011).

Precipitation amount and simultaneous event mean air temperature were recorded hourly at the Akkem station from 21 July 2002 to 23 July 2003. Water samples from each precipitation event were collected for determination of stable isotope ratios (δ^{18} O, δ D).

3. DATING TECHNIQUES

To establish the initial age/depth scale, we used: (1) a clear tritium peak attributed to the 1963 global atmospheric tritium maximum at the upper part of the core; (2) ¹⁴C dating from discrete POC samples (at the bottom part of the core); (3) a steady-state glacier flow model for layer thinning

(Raymond, 1983; Thompson and others, 1989, 2000; Yao and Yang, 2004; Davis and others, 2005; Kaspari and others, 2008); (4) identification of seasonal signals in annual layers through analyses of stable isotope distribution to a depth of 51 m w.e. with discrepancy <10% and below 51 m w.e. with discrepancy exceeding 10%; and (5) stratigraphy to a depth of 62 m w.e.; below 62 m w.e., the discrepancy between dating by stratigraphy and by steady-state glacier flow modeling exceeds 10%. Validation of dating was developed through identification of distinct layers, including significant volcanic eruptions, forest fires, the Tunguska meteorite event, and a notable dust storm in 1842 likely caused by extremely strong winds, as described in Chikhachev's journey to the Eastern Altai (Henderson and others, 2006; Malygina, 2009).

The interpolation/extrapolation between ¹⁴C radioactivity marks was based on fitting a steady-state glacier flow model to the counting age/depth profile through a least-squares method, taking into account validating events.

3.1. Tritium concentrations (Fig. 4; Table 1)

Ice-core chronology was refined using radioactivity measurements (Naftz and others, 1996; Schwikowski and others, 1999; Pinglot and others, 2003). The analyzed tritium concentrations with depth exhibit several notable peaks consistent with past nuclear testing. The earliest tritium peak (68.5 TU at 15.49 m w.e.) was attributed to the first historical nuclear testing maximum in 1958, while the subsequent and largest peak (reaching 772 TU at 14.11 m w.e.) was attributed to the time of maximum recorded nuclear detonations from 1962 to 1963 (Carter and Moghissi, 1977; Beck and Bennett, 2002). Five sampled radioactive horizons related to 1963 have at least three times higher values than any others with one maximum of 772 TU. The largest peak as well as minor subsequent tritium peaks (119.6 TU at 12.82 m w.e. and 127.4 TU at 11.04 m w.e.) are consistent with relative tritium concentration peaks preserved in the East Belukha (Olivier and others, 2004) during the late 1960s and early 1970s, respectively.

3.2. ¹⁴C measurements of POC (Figs 4 and 5a; Table 1)

Four depths were chosen for ¹⁴C measurements. The deepest measured horizon at 145.2 ± 0.1 m w.e. depth (0.665 m w.e. from the bedrock) corresponds to 9075 ± 1221 cal a BC, suggesting that Altai glaciers were formed during the YD. The next horizon at 142.8 ± 0.4 m w.e. (3.065 m w.e. from the bedrock) corresponds to 6197 ± 473 cal a BC, coincident with the sudden significant 8.2 ka cooling episode. Two other samples were obtained from the upper ice-core layers with sufficient organic carbon for radiocarbon dating. The corresponding ages were 135 ± 221 cal a BC at 134.6 m w.e. depth (11.2 m w.e. above the bedrock) and 790 ± 93 AD at 121.1 m w.e. depth (26.88 m w.e. above the bedrock) (Figs 4 and 5a). The dated age of a ¹⁴C measured layer was determined within the possible range of yearly deviation (i.e. ± uncertainty) according to ice flow modeled dating or other corresponding historical events such as significant volcanic eruptions (Table 1).

3.3. Stratigraphy (Fig. 2a)

Dating of the upper ice-core sections was preliminarily assigned by counting annual (summer) layers based on

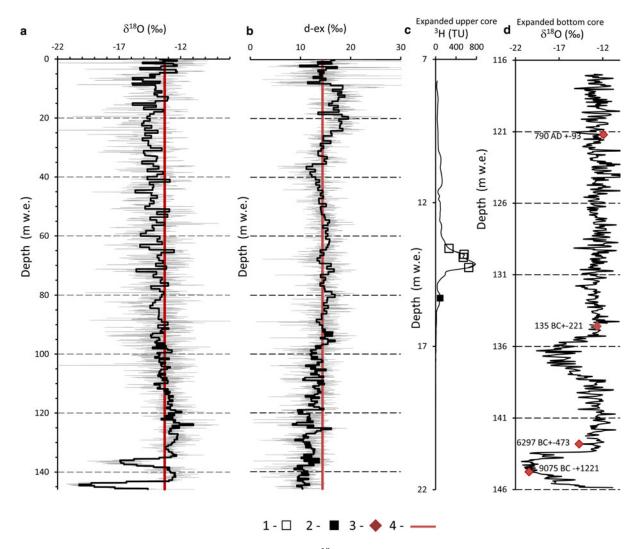


Fig. 4. (a) Oxygen stable isotope ratios and 1/0.5 m w.e. averages of δ^{18} O (‰) and (b) d-ex (‰) from the Bl2003 ice core with (c) radiogenic isotope records of 3 H (TU) at the top of the ice core, and (d) four 14 C records at the bottom of ice core. 1 - 3 H records related to 1958; 3 - 14 C records; 4- mean of δ^{18} O and d-ex for ReWP.

detailed visible inspection of core stratigraphy. This technique was used successfully for the Greenland GISP2 ice core (e.g. Alley and others, 1993; Meese and others, 1997), for dating ice cores recovered from the Dunde and Guliya ice caps (Thompson and others, 1989), and also for shallow Tien Shan and Altai ice cores (Aizen and others, 2005, 2006). Due to the absence of regular/annual visible dust layers in Belukha ice cores, stratigraphic layer counting was achieved by identifying thin transparent ice interlayers related to summers radiation crusts. Melt percentage was found to be \sim 7% in the upper 30 m w.e. of the core (Aizen and others, 2005; Joswiak, 2008), indicating an absence of percolation (Koerner and Fisher, 1990). Okamoto and others (2011) also reported that percolation was absent based on detailed stratigraphic analysis of ice-core layers (the upper 33 m w.e.) coincident with maximum air temperatures.

3.4. Variability in stable isotopes (Figs 2a, 4, 5 and 6)

Ice-core chronology was also refined by counting annual layers (Figs 2a and 5b) based on stable isotope variability/seasonality (e.g. Taylor and others, 1992). The δ^{18} O and δ D ratios were analyzed to determine the overall behavior of

the stable isotope ratios with depth/time (Fig. 4). Stable isotope values in glacial cores are determined by air temperature during snowfall, seasonal distribution of precipitation, transport, mass exchange and distillation history of an air mass.

Because the Altai Mountains are located in the center of the Eurasian continent, precipitation amount during a snowfall event is not significant. Therefore, a precipitation amount effect (Dansgaard, 1964) is assumed to be absent, and distribution of stable isotope values in the ice core mainly reflects seasonal air temperature distribution (correlation up to 0.7; Aizen and others, 2006), which is notably pronounced in intercontinental regions. Identification of annual accumulation layers in the ice core was based on the extreme values of δ^{18} O, as minimum winter and maximum summer air temperatures, which are distinctive characteristics of the Altai meteorological regime (Aizen and others, 2005). The stable isotope records from the surface to 51 m w.e. (Fig. 2a) yield well preserved seasonal signals of δ^{18} O.

The $\delta^{18}O-\delta D$ relationship in the Bl2003 ice core reveals a similar slope to the co-variance (i.e. 8) of the Global Meteoric Water Line indicating a similar initial relationship in fractionation factor pointing to the absence of percolation in the

 Table 1. Historical events recorded in Bl2003 ice-core from the Belukha Plateau, Siberian Altai

z m w.e	lons $\mu \text{EqL}^{-1}; \delta^{18} \text{O} \%; \text{OCppb}$	a/period/event		Comments			
0.012; 1.0	K ⁺ = 8; K ⁺ = 14.3 2003 ff: 73 % Siberia; 2002 ff: Yakutiy		Industrialization: Modern (MoWP)	2 006 632 ha of burned areas (15)			
3.4	$SO_4^{2-} = 53.9$; $Ca/SO_4 = 0.6$	1991 (June) er: Pinatubo, Philippines; VEI 6	Depleted isotopes (δ^{18} O = -19.7%) after eruption				
3.4 10.6	$K^+ = 2.8$ $K^+ = 4.1$	1991 ff 1974 ff	forest fire: 1 126 000 ha (15) forest fires 1 384 000 ha (15; 17)				
14.1 15.5	$^{3}H = 772 \text{ TU}$ $^{3}H = 68.5 \text{ TU}$	1963 max nuclear detonations 1958 first nuclear detonations	The largest nuclear detonations				
16.38	$SO_4^{2-} = 53.7$; $Ca/SO_4 = 0.6$	1956 er: Bezymianny, Kamchatka;VEI5		1963 (16) Bl2003: Large increase in sulfates and nitrates in MoWP, and they have been decreased in ReWP			
17.8	Elevated SO ₄ ²⁻ NO ₃ ⁻ level	1951 beginning of Industrialization in Siberia, USSR		III ICVVI			
24.9; 26.7 27.56 28.5	$K^{+} = 1.6 K^{+} = 1.0$ $SO_{4}^{2-} = 26.2$; $Ca/SO_{4} = 0.3$ $NO_{3}^{-} = 18.9$	1921 ff: Russia, Povolj'e; 1915 ff: Russia Pre- 1912 er: Novarupta, USA; VEI 6 industrialization 1908 Tunguska explosion event; Russia		12 500 000 ha (15) Air burst of a large meteoroic			
35.96	$SO_4^{2-} = 20.2$; $Ca/SO_4 = 0.8$	1883 er: Krakatoa, Indonesia;VEI 6	Little Ice Age (LIA)	comet Bl2003 depletion till the middle of 20th century			
41 45.14 46.25	$Ca^{2+} = 134.4$; $SO_4^{2-} = 22.2$ Depleted isotopes $SO_4^{2-} = 16.1$; $Ca/SO_4 = 0.3$	1842: dust storm (14) 1816: Year without summer (13) 1815 er. Mt. Tambora, Indonesia; VEI 7		1842: Extreme peaks in ions Bl2003: Depleted Isotopes LIA began in late Medieval times 1400 (10) in Europe; in 1480 in Siberia Teletskoe lake (11); around 1500 AD in			
47.74	$SO_4^{2-} = 22.6$; $Ca/SO_4 = 1.4$	1809 er:'unknown' or 1800 er. St. Helens, USA;VEI 5		China (12) Bl2003: Circa middle of 15th century – beginning the LIA			
52.96 55.4 62.1	$SO_4^{2-} = 12.9$; Ca/SO ₄ = 0.8 $SO_4^{2-} = 10.0$; Ca/SO ₄ = 0.6 $SO_4^{2-} = 7.5$; Ca/SO ₄ = 1.0	1755 er: Katla, S. Iceland; VEI 5 1739 er: Shokotsu, Japan; VEI 5 1707 er: Fuji, Japan; VEI 5		, ,			
66.37	$SO_4^{2-} = 11.5$; $Ca/SO_4 = 1.5$	1667 er: Shikotsu, or 1663 er. Usu, Japan; VEI 5					
68.9 70.2	$SO_4^{2-} = 13.7$; $Ca/SO_4 = 0.4$ $SO_4^{2-} = 5.5$; $Ca/SO_4 = 1.0$	1650 ± 10 er: Shiveluch, Kamchatka; VEI 5 1625 er: Katla, S, Iceland; VEI 5					
71.3 71.59	Depleted isotopes $SO_4^{2-} = 9.3$; $Ca/SO_4 = 0.4$	Circa 1601 1600 er.: Huaynaputina, Perú; VEI 6					
73.9 84.5	$SO_4^{2-} = 5.5$; Ca/ $SO_4 = 1.0$ $SO_4^{2-} = 20.8$; Ca/ $SO_4 = 0.6$	1580 er. Billy Mitchell, Bougainville; VEI 6 1480 er: St.Elena, USA VEI 5+ or 1477 er.: Bardarbunga, Iceland; VEI 6					
85.3 86.95 88.04	$SO_4^{2-} = 5.7$; $Ca/SO_4 = 0.9$ $SO_4^{2-} = 12.4$; $Ca/SO_4 = 1.2$ $SO_4^{2-} = 11.4$; $Ca/SO_4 = 1.3$	1471 er: Sakura-Jima, Japan; VEI 5 1452 ± 10 er: Kuwae; VEI 5+ 1442 er: Oshima; VEI 5					
102.3 104.16	$SO_4^{2-} = 10.5$; $Ca/SO_4 = 0.7$ $SO_4^{2-} = 8.7$; $Ca/SO_4 = 1.8$	1280 er: Quiloto, Ecuador; VEI 6 1262 er: Katla, S. Iceland; VEI 5. 1259 er:					
117.3	$SO_4^{2-} = 9.5$; $Ca/SO_4 = 1.3$	might be El Chichon, Mexico (9) 1000er. Changbaishan, China; VEI 7	Medieval Warm Period, MWP	Tree ring (7) from N. Fennoscandia – a warm period: 870–1100 AD; (8) relates the MWO Bl2003: MWP: circa 640–1100 AD. T was on average 0.46 °C			
121.1	OC = 68 ppb	790 ± 93 AD		higher than during ReWP			
123.2 123.98 124.57	$SO_4^{2-} = 7.2$; $Ca/SO_4 = 1.6$ $\delta^{18}O = -8.93\%$ $SO_4^{2-} = 8.9$; $Ca/SO_4 = 0.9$	800 ± 100 er: Churchill, Alaska; VEI 6 Highest enriched δ^{18} O corresponds to MWO 610 ± 50 er: Opala, Kamchatka; VEI 5+					
126.4	$SO_4^{2-} = 4.0$; $Ca/SO_4 = 2.0$	550 ± 10 er: Shiveluch, Kamchatka; VEI 5. 52	0 ± 10 er: Haruna,				
130.75 132.05 132.88	$SO_4^{2-} = 5.0$; $Ca/SO_4 = 1.5$ $SO_4^{2-} = 4.2$; $Ca/SO_4 = 2.5$ $SO_4^{2-} = 6.0$; $Ca/SO_4 = 3.0$	Japan, VEI 4+ 240 ± 100 er: Ksudach, Kamchatka; VEI 6 60 ± 200 er., Churchill, E. Alaska; VEI6 100 BC ± 50 er: Okmok, Aleutian Island; VEI	6				
134.6 ± 0.4	OC = 62.8 ppb 159	135 BC ± 221					

Table 1. (Cont.)

z m w.e	lons μEqL ⁻¹ ; δ ¹⁸ O‰; OCppb	a/period/event	Comments				
136.187	$SO_4^{2-} = 11.6 \text{ Ca/SO}_4 = 3.0$	1050 BC ± 500 BC Pinatubo, Philippines; VEI 6	Severe Centennial Drought, SCD	SCD significant cold (N. Africa, N. America, SE. Asia, 2400– 1700 a BC (6)			
136.31	$\delta^{18}O = -19.44\%$	Depleted isotopes-the lowest air temperatures	. ,				
137.251	$SO_4^{2-} = 13.7$; $Ca/SO_4 = 2.7$	1610 BC ± 14 er: Santorini, Greece; VEI 7	Bl2003: isotopes depletion ~2000 to 600 a BC				
138.095 138.46	$SO_4^{2-} = 26.6$; $Ca/SO_4 = 2.3$ $SO_4^{2-} = 30.3$; $Ca/SO_4 = 3.0$	1860 BC St. Helens, USA; VEI 6 1900 BC ± 150 er: Black Peak, Alaska; VEI 6					
139.025 141.831	$SO_4^{2-} = 22.3$; $Ca/SO_4 = 2.9$ $\delta^{18}O = -10.53$	2040 BC \pm 100 er: Longlsl, N.Guinea;VEI6 Circa 5100–4600 a BC max δ ¹⁸ O during HCO	Bl2003: HCO from circa 6500 to 3600 a BC				
141.926	$SO_4^{2-} = 15.0$; $Ca/SO_4 = 3.6$	4000 ± 200 BC er: Masaya, Nicaragua; VEI 6	Optimum, HCO	Bl2003: enriched on 10.8‰ from YD			
142.088 142.65	$SO_4^{2-} = 24.7$; $Ca/SO_4 = 3.3$ $SO_4^{2-} = 21.1$; $Ca/SO_4 = 5.6$	5500 ± 100 BC er: Mashu, Japan; VEI6; 5700 BC er. Kamchatka, Russia; VEI 6 or 5677 ± 150 BC er: Crater Lake, Oregon; VEI 7					
142.8 ± 0.4	$OC = 47.2 \text{ ppb } \delta^{18}O = -14.7$	6197 ± 473 BC; 8.2 ka cooling episode	Cold dry phase (2, 3). Bl2003: isotopes depletion				
143.08	$SO_4^{2-} = 117.8$; $Ca/SO_4 = 2.1$	6200 ± 100 BC er: Kyushu, Japan; VEI6 or	CA deserts were forested due to rainfall, warm temperate (4, 5)				
143.27 143.4	δ^{18} O: from -20.3 to -13.39 SO ₄ ²⁻ = 140.9; Ca/SO ₄ = 1.4	6400 a BC Abrupt warming event (AWE2): 6440 ± 25 BC er: Kuril L., Kamchatka; VEI7		, , , ,			
143.47 143.82	$\delta^{18}O_{min} = -20.3$ $\delta^{18}O$: from -21.3 to -16.55	6900–6600 BC Pre Boreal Oscillation event Circa 7300 a BC Abrupt warming event (AW	Cool PBO sharp rise of air temperature in Europe (1)				
143.92 144.008	$SO_4^{2-} = 140.9$; $Ca/SO_4 = 1.4$ $SO_4^{2-} = 192.4$; $Ca/SO_4 = 1.3$	7420 ± 200 er: Fisher, Aleutian Isl.; VEI 6 7460 ± 150 BC er: Pinatubo, Philippines; VE	El 6	Bl2003: AWE1			
	$SO_4^{2-} = 50.3$; $Ca/SO_4 = 0.7$	7480 ± 80 BC er: Lvinaya past, Kuril Isl.; VEI	16+	Bl2003: beginning PB; huge increase of the ions			
144.04 145.2 ± 0.1	$\delta^{18}O_{min} = -21.3$ OC = 47.2 ppb	Circa 7800 BC 9075 ± 1221 BC	Younger Dryas, YD	The most depleted isotopes			
145.236	$SO_4^{2-} = 394.8$; $Ca/SO_4 = 1.1$	9500 ± 300 BC er: Khangar, Kamchatka		Massive caldera-forming eruption			
145.75		Circa10 950 a BC		Sharp drop of isotopes; huge increase of ions			
145.865		BL2003 Bedrock: Altai glaciers regenerated					

er., eruption; VEI, volcanic explosivity index; ff, forest fire.

1. Johnsen and others (1997); Kobashi and others (2008); 2. Zoller (1960); 3. Alley and others (1997); Alley and Ágústsdóttir (2005); 4. Winkler and Wang (1993); 5. Koshkarova and Koshkarov (2004); 6. Claussen and others (1999); Kalugin and others (2005); 7. Briffa and others (1990); 8. Mann and others (2009); 9. Palais and others (1992); 10. Mayewski and others (1993); Meese and others (1997); Bradley (2000); Bradley and others (2003); 11. Andreev and others (2007); Butvilovskii (1993); Jacoby and others (1996); Ovchinnikov and others (2000); 12. Li and Ku (2002); 13. Stothers (1984); 14. Olivier and others (2006); 15. Vorob'ev and others (2004); 16. Carter and Moghissi (1977); Beck and Bennett (2002); 17. Valendik (1996); Eruptions dates were taken from the Global Volcanism Program (http://www.volcano.si.edu/world/largeeruptions.cfm) and (Zielinski, 1995).

Bl2003 ice core. For different time periods, the slope varied from 8.4 to 6.1. Slopes do not approach typical sublimation/evaporation line slopes ~'5' (Clark and Fritz, 1997) (Table 2). It is unlikely that evaporative/sublimation changes that could occur at site would significantly affect the preserved ice-core records.

3.5. A steady-state glacier flow model for layer thinning (Figs 7a-c)

A steady-state glacier flow model was used to determine the ice age, t (a) in the Altai ice core as a function of depth. We applied the numeric modeling of annual ice thickness, L(z) with depth initially presented by Raymond (1983) and

implemented by Thompson and others (2000), Yao and Yang (2004), Davis and others (2005) and Kaspari and others (2008), where

$$L(z) = Ac(1 - z/H)^k \tag{1}$$

and

$$t = \frac{H^k}{[(k-1)Ac][1/(H-z)^{k-1} - 1/H^{k-1}]}$$
 (2)

H (145.867 m w.e.) and *z* are ice equivalent thickness and depth. Ac (0.344 m w.e.) is the original layer thickness as determined from the present thickness of annual layers, e.g.

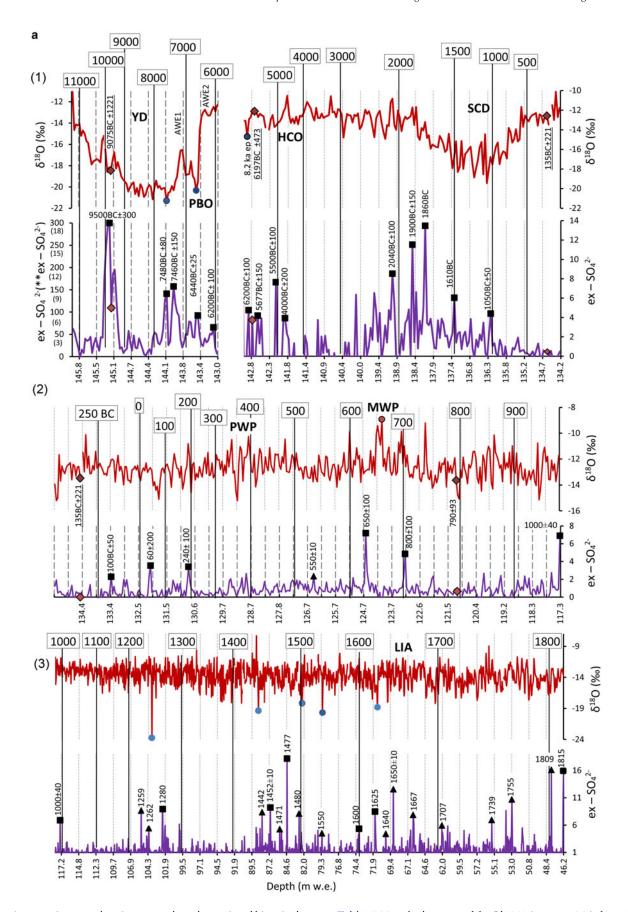


Fig. 5. Ice-core isotope-chemistry records and associated historical events (Table 1) (a) at the low part of the Bl2003 ice core: (1) is from 145.8 to 134.2 m w.e., (2) is from 134.5 to 117.3 m w.e., (3) is from 117.3 to 46.2 m w.e., and (b) at the upper part of the Bl2003 ice core. Stable isotope records of $\delta^{18}O$ (‰) are red, non-dust sulfate absolute, ex-SO₄²⁻ (μEq L⁻¹) and normalized, **ex-SO₄²⁻ (Eqn (4)) and *ex – SO₄²⁻ (Eqn (5)) fraction records are violet, major ions of Ca²⁺, NO₃⁻, K⁺ (μEq L⁻¹) are black and radiogenic isotope of ³H (TU); 1 is ¹⁴C records; 2₁, 2_h are extreme low/high temperatures; 3₅ and 3_{≥6} are referred volcanic eruptions with corresponding VEI = 5 and VEI = 6 or 7; 4 is Tunguska explosion; 5 is forest fires; 6 is ³H records; 7 is strong dust storm.

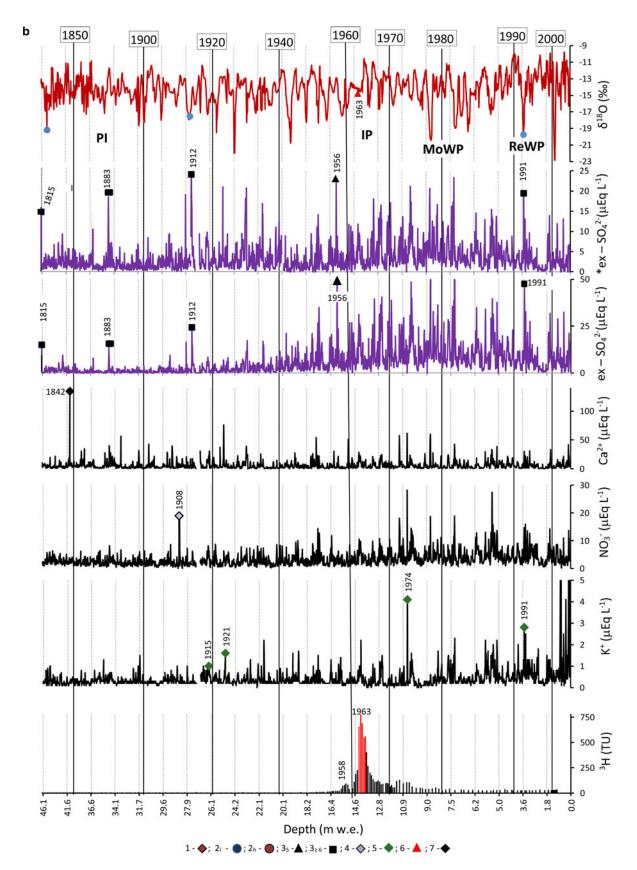


Fig. 5. (continued)

from Eqn (1) the snow pit stratigraphy seasonal layers for 2002, or from Eqn (2) the thickness of snow/firn/ice between two annual timelines, i.e. for the period, 1963 (3 H marked event; Section 2.1) to the present. k (1.53) is the constant determined by least squares, to minimize the discrepancy in dating.

3.6. Peaks in sulfate concentrations/volcanic eruptions

Volcanic eruptions are also used as reference horizons to validate the dating (Zielinski and others, 1994; Zielinski, 1995; Siebert and others, 2010; Moore and others, 2012). For

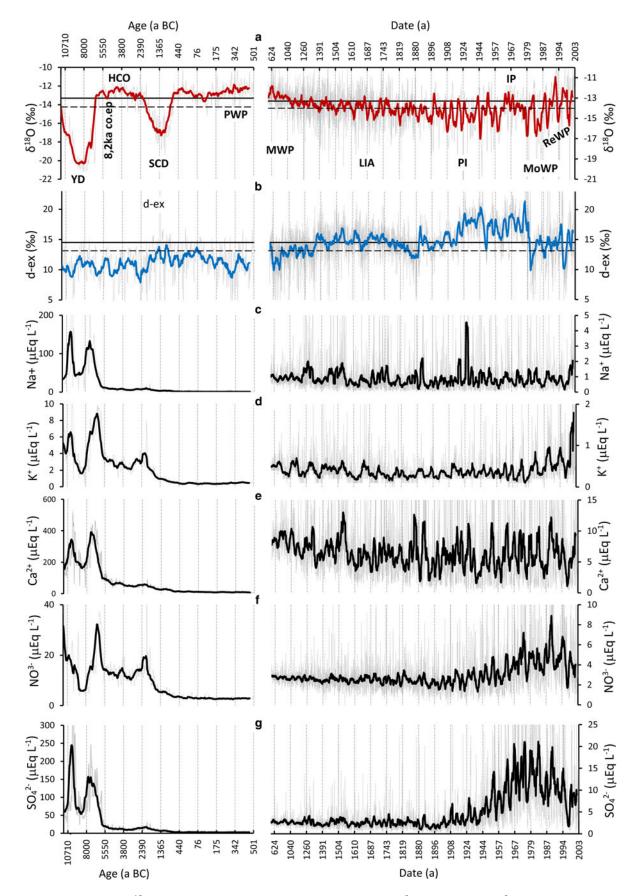


Fig. 6. Dated (a) stable isotope, $\delta^{18}O$ (‰), (b) d-ex (‰) and major ions of (c) Na⁺, (d) K⁺, (e) Ca²⁺, (f) NO₃⁻ and (g) SO₄²⁻ records with 10-record and 30-record (bold) moving averages and averages for the ReWP (direct solid black) and for the MoWP from (dashed black) from the Bl2003 ice core.

inferring volcanic source analysis, we use the Smithsonian Global Volcanism Program database of Holocene volcanism (Siebert and Simkin, 2002). We considered significant volcanic eruptions with a volcanic explosivity index (VEI) ≥ 5

and focused on eruptions that are most likely recorded in Siberian Altai ice-core records, e.g. from Kamchatka, Japan (Table 1). Significant anomalies ($\geq 2\sigma$) of sulfate concentrations associated with volcanic eruptions were considered

Mean $\delta^{18}O$ Circa years d-ex Slope ReWP 1993-2003 14.4 7.6 -13.3MoWP 1973-2003 -14.113.9 7.7 1951-1973 -14.217.4 8.4 ы 1900-1950 -14.616.7 8.1 LIA 1550-1900 AD -14.214.4 8.0 **MWP** 700-1150 AD -12.812.2 6.2 SCD 2000-1000 BC -16.512.6 6.8 **HCO** 6500-3600 BC -12.710.2 6.1 7100/7800-10 950 BC PB0/YD -18.510.7 7.6

Table 2. Mean characteristics of the stable isotope distribution for the different periods of the Altai glacier existence

as markers for validation of the depth/age scale. However, significant anomalies of sulfate concentrations, SO_4^{2-} , may also be associated with Ca^{2+} (e.g. gypsum and/or anhydrite), which originates from evaporite deposits. If gypsum and/or anhydrite were the primary soluble compound delivering SO_4^{2-} to the site, then a Ca^{+2}/SO_4^{2-} equivalence ratio >1 would be expected. This was not the case for the markers of volcanic eruptions. We considered significant anomalies in sulfate (SO_4^{2-}) with Ca^{2+}/SO_4^{2-} equivalence ratios <1 above 46.25 m w.e. (Mt. Tambora eruption in 1815).

Below 46.25 m, e.g. during the LIA and earlier, the Ca^{2+} background and Ca^{2+} extremes were more significantly increased than SO_4^{2-} . Therefore, to reveal the maxima related to volcanic eruptions we used only the non-dust sulfate fraction (Eqn (3); ex- SO_4^{2-}) (Figs 5a and b; Table 1) as utilized for the Bl2001 ice-core dating (Olivier and others, 2006).

$$ex-SO_4^{2-} = SO_4^{2-} - n Ca^{2+},$$
 (3)

**ex-SO₄²⁻ = SO₄²⁻/20-
$$n$$
 Ca²⁻/45 (below 142.8 m w.e.), (4)

*ex-
$$SO_4^{2-} = SO_4^{2-}/2.1 - n \text{ Ca}^{2-} \text{ (above 17.8 m w.e.)}, (5)$$

where n is the average ratio between SO_4^{2-} and Ca^{2+} concentrations for the period, 1815-99 with well-calibrated records of non-volcanic events. The value of n was reported to be 0.21 in the BL2001 ice core (Olivier and others, 2006) and the same value was applied for calculation of the non-dust sulfate fraction (ex- SO_4^{2-}) (Eqn (3)) for volcanic eruption indicators in the present study.

For bottom ice-core sections (below 142.8 m w.e.), SO_4^{2-} and Ca^{2+} background and extreme concentrations were significantly elevated. Therefore, to compare bottom records with the other part of the ice core, the SO_4^{2-} and Ca^{2+} bottom records were normalized by an average basic noise factor of '20' and '45' (Eqn (4)), respectively (Fig. 5a), then the peaks in the non-dust sulfate fraction (**ex- SO_4^{2-}) were the same order as those in the other periods, e.g. pre-industrial. Average basic noise was estimated as a ratio between background means during periods of elevated the SO_4^{2-} and Ca^{2+} concentration (i.e. YD) and background means during the pre-industrial period (PI).

For the upper part of the core (above 17.8 m w.e.), the SO_4^{2-} background and SO_4^{2-} extreme concentrations were

also increased (on average 2.1 times) compared with the lower part of the core (e.g. PI). A similar procedure of normalization with an average basic noise factor of 2.1 (Eqn (5)) was applied. After normalization peaks in sulfate (*ex- SO_4^{-1}) were the same order as those for the pre-IP (Fig. 5b).

Intensive growth in sulfate from the background with a simultaneous decline in the Ca^{2+}/SO_4^{2-} equivalence ratio relative to adjacent records, as well as the non-dust sulfate fraction maxima (Eqns (3–5)), were also considered when assigning volcanic eruptions. The appearance of significantly depleted isotopes follows in many cases after the sulfate anomalies associated with volcanic eruptions (Fig. 5). This illustrates the impact of strong volcanic eruptions on the temporal decrease of air temperatures.

3.7. Peaks in biomass burning

The large forested areas of western Siberia and northeastern Kazakhstan are located directly upwind from the Belukha Plateau, and aerosols injected to the atmosphere by large forest fires are preserved in Altai glacier ice. Ice-core records have been used as a proxy for large fire activity by examining the variability of soluble major ions associated with smoke from fire plumes (e.g. Whitlow and others, 1994; Yalcin and others, 2006; Olivier and others, 2006). Eichler and others (2011) demonstrated that K⁺ and NO₃ are suitable proxies for biomass burning and the temporal and spatial distribution of forest fires over Russia, including Siberia, is well known. The largest forest fires in the Altai Mountains and Southwestern Siberia were recorded in 1921, 1974, 1991 and 2003 (Valendik, 1996; Vorob'ev and others, 2004). Peaks in K⁺ potentially associated with forest fires (Fig. 5b; Table 1) were also used to validate dating at the upper part of Bl2003 ice core.

3.8. Identification of distinct layers: Tunguska meteorite event and a notable dust storm

The Tunguska explosion event (1908) corresponds to a significant nitrate peak (Henderson and others, 2006) in the B12003 core (at 28.5 m w.e. depth; Fig. 5b). The most pronounced visible horizon through stratigraphy analysis in the upper part of the Bl2003 ice cores is a thick dust layer dated to 1842 (Henderson and others, 2006; Malygina, 2009) at 41 m w.e. signaled by a peak in calcium (Fig. 5b). These two events were also used to calibrate dating in the upper part of the Bl2003 ice core.

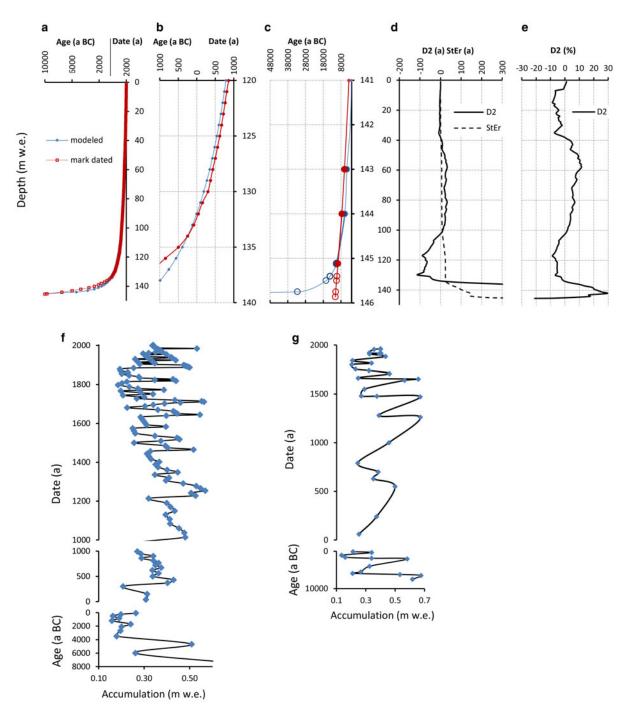


Fig. 7. (a) Modeled and mark-dated age/depth profiles of the Bl2003 ice core with (b) extended bottom part from 120 to 140 m w.e. and (c) from 141 to 145.87 m w.e. (d) The standard error profile, StEr (a) and (d and e) discrepancy, D2 (a and %) between modeled and mark-dated Bl2003 ice-core records. Dating validation through annual accumulation estimated for (f) each meter of w.e. and (g) marked events.

3.9. Discrepancy, uncertainty and standard error

Discrepancy-1 (D1) over the upper part of the core (until 62 m w.e.) is the difference in years of an horizon dated by different techniques, i.e. tritium picks, stratigraphy/isotope analysis, and validated through volcanic eruption marks (Table 3). Discrepancy-2 (D2), considered along the Bl2003 ice core (Figs 7d and e), is estimated based on comparison between dated age/depth profile (radioactive measurements, counting annual ice layer through stratigraphy, stable isotopes, etc.) and the calculated profile using a steady-state glacier flow model for layer thinning (Section 3.5) with validation through volcanic eruption events. The absolute discrepancy (Fig. 7d) is estimated as the absolute difference in years of a horizon. Relative discrepancy is the

ratio between the difference in dated years (D2) and the number of years from the surface (Table 3).

Uncertainty-1 (U1), below 121.1 m w.e. is based on the uncertainty of validation referenced by volcanic eruption dating (Siebert and Simkin, 2002). Uncertainty-2 (U2) is the uncertainty in ¹⁴C measurements of the four POC horizons and values of uncertainty interpolated between the four ¹⁴C measured horizons. Absolute and relative values of uncertainty are estimated in years and percent relative to mean year of a horizon (Table 3).

The standard error, StEr (a) of dated Bl2003 ice-core records relative to modeled results is estimated beginning in 1963 (for the period 1963–2003) and earlier (deeper) (Table 3; Fig. 7d). Determination of the 1963 tritium peak

Table 3. Measured and modeled age, and discrepancy (D1, D2), uncertainty (U1, U2) and standard errors (StEr) in dating of the Bl2003 ice core

Depth m w.e.	Event	Measured and validated age determinant	Measured Date	D1 a	Modeled	D2 a	%	Age Bl2003	U1 a	U2 a	U2 %	StEr a
m w.e.			Date	d	age	а	/0	B12003	а	d	/0	a
3.4	Pinatubo er.	Ca/SO_4 ; ex- SO_4^{2-}	1991		1990.9	0	-1	1991				
		Stratigr/ δ^{18} O	1991									
14.1	Max nuclear detonations	³ H	1963	1	1961.5	-1.5	-3.7	1963				0.5
		Stratigr/ δ^{18} O	1964									
15.2	First nuclear detonations	δ^3 H	1958	2	1954	-4	-7	1958				0.7
		Stratigr/ δ^{18} O	1960									
27.56	Novarupta er.	Ca/SO_4 ; ex- SO_4^{2-}	1912	4	1908	-4	-3.9	1912				1.2
		Stratigr/ δ^{18} O	1916									
28.5	Tunguska event	NO_3	1908	4	1905	-3	-3	1908				1.3
		Stratigr/δ ¹⁸ O	1912									
35.96	Krakatoa er.	Ca/SO_4 ; ex- SO_4^{2-}	1883	6	1874	-9	-8	1883				1.6
		Stratigr/ δ^{18} O	1889									
41	Dust storm	Ca ²⁺	1842	5	1850	8	6	1842				2.5
		Stratigr/δ ¹⁸ Ο	1847									
46.25	Tambora er.	Ca/SO_4 ; ex- SO_4^{2-}	1815	9	1822	7	7	1815				2.9
		Stratigr/ δ^{18} O	1824									
47.74	Unknown er.	Ca/SO_4 ; ex- SO_4^{2-}	1809	12	1814	15	8	1809				3.7
		Stratigr/ δ^{18} O	1805									
62.1	Fuji er.	$ex-SO_4^{2-}$	1707	16	1730	23	8	1707				6.2
		Stratigr	1723									
66.37	Usu/Shikotsu ers.	ex-SO ₄ ²⁻	1665		1691	24	8	1667				6.1
71.59	Huaynaputina er.	ex-SO ₄ ²⁻	1610		1633	23	9	1610				6.4
84.5	Bardarbunga er.	$ex-SO_4^{2-2}$	1477		1515	35	7	1480				7.1
102.3	Quiloto er.	ex-SO ₄ ²	1271		1283	3	0	1280				9.9
104.16	El Chichon	ex-SO ₄ ²	1255		1248	-11	-1	1259				11.2
117.3	Changbaishan er.	ex-SO ₄ ²	1000		921	-79	-9	1000				22.7
121.1 ± 0.3		OC ppb	790 ± 93		744	-66	-6	810		186	15	24.0
123.2	Churchill er.	ex-SO ₄ ²⁻	800 ± 100		650	-70	-5	720	200	227		24.1
124.57	Opala er.	ex-SO ₄ ²	610 ± 50		565	-75	-5	640	100	253		24.1
130.75	Ksudach er.	ex-SO ₄ ²	240 ± 100		156 AD	-84	-4	240	200	370		24.3
132.05	Churchill er.	ex-SO ₄ ²	$60 \text{ AD} \pm 200$		6 BC	-46	-2	40 AD	400	394		24.5
132.88	Okmok er.	ex-SO ₄ ²	100 BC ± 50		115 BC	-35	-2	80 BC	100	410		24.8
134.6 ± 0.3		OC	135 BC ± 221		326 BC	4	0	330 BC	100	442	20	26.0
134.0 ± 0.3	Pinatubo er,	ex-SO ₄ ²⁻	1050 BC ± 500		570 BC	330	12	900 BC	1000	540	20	48.3
137.251	Santorini er.	ex-5O ₄ ex-SO ₄ ²	1610 BC ± 14		850 BC	740	19	1590 BC	28	605		67.0
137.231	St.Helens er.	ex-5O ₄ ex-SO ₄ ²	1860 BC		1020 BC	840	18	1860 BC	20	657		76.6
138.095		ex-5O ₄ ex-SO ₄ ²⁻	2040 BC ± 100		1310 BC	790	19	2100 BC	200	657 714		76.6 91
139.025 142.8 ± 0.4	Long Isl er.	ex-sO ₄ OC			4685 BC	790 1315	16	6000 BC	200	946	11	91
142.0 ± 0.4	ŧ∠	UC	$6297 \text{ BC} \pm 473$		4003 BC	1315	10	DOUG BC		940	1.1	

275.0 327.3 451.0 2442 2572 \sim 10 950 BC 11 170 BC 7400 BC 9700 BC 0 260 BC 0450 BC 9800 BC -3925 -6050-180721 635 5845 BC 10411 BC 11 607 BC 14 815 BC 16 500 BC 32 585 BC 303 070 BC Modeled \Box $9075 BC \pm 1221$ $9500 \pm 300 \text{ BC}$ 7480 BC ± 80 Measured Measured and validated age determinant $ex-SO_4^2$ -OC Lvinaya past er. Khangar er.
 Table 3. (Cont.)
 $|45.117 \pm 0.12|$ 144.008 145.865 145.75 m w.e. 145.5 Depth 145.4

D1 is discrepancy between dating through tritium marks (^3H) , sulfate $(exSO_4^2)$ or nitrate (NO_3^2) concentration marks and dating though stratigraphy or stable isotope annual signals $(Stratign/8^{18}O)$. D2 is discrepancy between modeled uncertainty in delion3 ice core; U1 is uncertainty in determining the date of marked volcanic eruption; U2 (bold font) is uncertainty in dating through four marks of ¹⁴C. U2 (Italic font) is related to interpolated uncertainty petween U2 marks. StEr, (a) is standard error between dated Bl2003 ice-core records and modeled results. through the seasonal signal in isotope/stratigraphy analysis yields a discrepancy of 1 year. Comparison of modeled depth/age with 1963 radioactive markers yields a discrepancy (D2) within 1.5 years, i.e. ~3.7% of the 40 years period from 1963 to 2003. StEr of dated Bl2003 ice-core records relative to modeled (Eqn (2)) is estimated as 0.5 year from 1963 to 2003 (Table 3).

Discrepancy (D1) is 4 years at the depth of the local sulfate peak (27.56 m w.e.) as attributed to the 1912 Novarupta eruption (Table 3). Validation of modeled dating through dating by $\exp SO_4^{2-}$, yields a discrepancy within 4 years, i.e. ~4%, at the 1912 horizon. Depth 117.3 m w.e., modeled to 1000 AD is validated through the Changbaishan eruption, yielding a discrepancy of 9% between modeled dating and validation through $\exp SO_4^{2-}$.

The discrepancy between dated ice-core and modeled profiles is <10% above 135 m w.e. (till ~330 a BC) in the Bl2003 ice core (Table 3; Fig. 7e). Standard error between dated and modeled ice-core records at 135 m w.e. is 26 years.

Below 135 m w.e. the discrepancy increased, reaching a maximum at the bottom. Until 145.4 m w.e. (~10 900 BC) the discrepancy (D2) in dated ice-core records is within the values of uncertainty (U2) of ¹⁴C measurement (Table 3). The discrepancy does not exceed 6% at three radiocarbon marked horizons. The discrepancy in dating through radiocarbon marks and modeled dating could be explained by a deviation in accumulation rate (Fig. 7f and g) from modeled accumulation (0.344 m w.e.) during periods of variable Altai accumulation rate history.

4. ISOTOPE/AIR TEMPERATURE RELATIONSHIPS

The variability of the stable isotope records from ice cores is used to estimate isotope/air temperature relationships. We examined isotope data from 136 precipitation events collected year-round at the Akkem meteorological station with corresponding mean air temperature during precipitation events. Eighty one events occurring during negative temperature periods at the Akkem station were selected.

The first step: The relationship between mean air temperatures during precipitation (T_{pr}) and $\delta^{18}O$ at Akkem station, $T_{pr.}=0.9\delta^{18}O+12.1$, was adjusted using the transfer function:

$$T_{\rm pr.} = 0.9(\pm 0.08)\delta^{18}O + 3.2 R^2 = 0.7 \text{ (at } \alpha = 0.05)$$
 (6)

with air temperature lapse rate, -0.43 °C ($100 \, \text{m}^{-1}$). We assume the isotopic composition of the precipitation deposited at the Akkem station is equivalent to the isotopic composition of the precipitation deposited at the Belukha Plateau. The air temperature lapse rate was obtained based on air temperatures measurements at AWS and Akkem station during the precipitation events. The standard error in air temperature during precipitation events modeled through stable isotope ratio in precipitation is estimated at $2.7 \, ^{\circ}$ C.

The second step: The Siberian Altai is located at the center of the Eurasian continent (Fig. 1) under the strong influence of the Siberian High (SH) and westerly jet stream. In winter, the SH blocks advection of fresh water transport, while in the warm season when the SH is weak maximum precipitation occurs throughout the Altai glacier region (Köppen climate classification). Currently, 86% of the annual precipitation in the Altai Mountains occurs during the warm season from May to October (Aizen and others, 2005). The warm season is clearly when maximum precipitation occurs, due to the

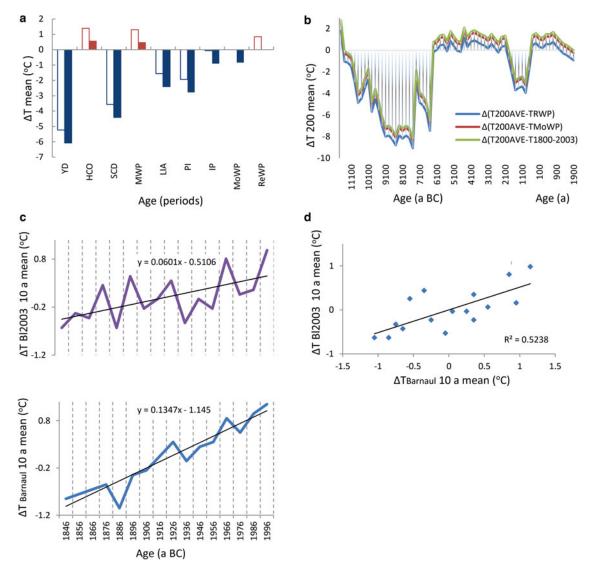


Fig. 8. (a) Average estimations on reconstructed air temperature deviations , ΔT , (°C) from the Recent (filled column: red is for positive and blue is for negative deviations) and Modern (not filled) Warm Periods for the different historical periods. (b) Bicentennial deviations of reconstructed air temperature from the Recent (green) and Modern (red) Warm Period mean of air temperatures and the last bicentennial mean (blue). (c) Decadal mean deviations from the last decadal mean of air temperature reconstructed from Bl2003 ice-core records and from Barnaul Station. (d) Correlation between deviations from the last decadal mean of decadal air temperature means at the Barnaul Station and reconstructed from the Bl2003 ice-core records.

'blocking' effect of the SH, which decreases precipitation during the cold seasons. Therefore, stable isotopes in ice-core records are biased toward warm season air temperatures, i.e. air temperature during precipitation events. The information recorded in Bl2003 ice core during the cold season is limited.

To take into account air temperatures without precipitation, a relationship between annual air temperature during precipitation ($T_{\rm pr}$) and mean annual air temperature ($T_{\rm reconstr}$) (Eqn (7)) was developed based on long-term data from Akkem station for the period, 1951–2001:

$$T_{\text{reconstr}} = -0.055 (T_{\text{pr}})^2 + 0.012 T_{\text{pr}} - 11.234$$

 $R^2 = 0.52,$ (7)

where $T_{\rm pr}$ is calculated as the mean annual precipitation-weighted temperature, $\sum kT$, k is the share of monthly amount of precipitation in the annual total and T is the mean monthly temperature. The standard error of mean annual air temperature, reconstructed from the mean annual air temperature during precipitation, is estimated at 0.68 °C.

Validation of the estimations in reconstructed air temperature deviations was achieved using the deviations of the decadal annual mean air temperatures from the average for the period, 1841-2001 from the Barnaul station. The decadal air temperature deviation variability at Barnaul station is similar to the variability in reconstructed decadal means of air temperature deviations from Bl2003 ice-core records (Fig. 8c) and the correlation is 0.52 for 16 decadal means (Fig. 8d). The tendency of increased/decreased air temperatures in the Bl2003 ice-core records is in accordance with Barnaul station data, while the amplitude of variability in air temperature deviations at the Barnaul station is insignificantly lower than in ice-core records. The long-term trend in air temperature deviations is more intense at the Barnaul station (0.13 °C (10 yrs⁻¹)) than revealed from Bl2003 ice-core records $(0.06 \, ^{\circ}\text{C} (10 \, \text{yrs}^{-1}))$.

5. ISOTOPE/d-ex RELATIONSHIP

Analysis of the main synoptic patterns that deliver moisture to the Altai Mountains reveals several clusters of moisture origin (Aizen and others, 2005, 2006), e.g. moisture originating over the Atlantic Ocean formed accumulation with d-ex values ranging from 7 to 14‰ and intermediate d-ex values of 10‰. Accumulation with d-ex records <7‰ is formed by moisture originating from the Pacific Ocean or the Northern Atlantic Ocean depending on δ^{18} O. That is, moisture enriched in δ^{18} O is generally derived from the Pacific Ocean, while moisture depleted in δ^{18} O is generally derived from the northern Atlantic or Arctic Oceans. The d-ex values over 14‰ are typical of re-evaporated moisture from southwestern regions, e.g. Caspian, Aral and Black seas (Froehlich and others, 2002; Aizen and others, 2005, 2006).

6. NET ACCUMULATION

Snow/firn/ice densities (Fig. 2) and annual layer modeled thinning coefficients were used to establish cumulative and w.e. depth profiles. The visual stratigraphy, depths of peaks in tritium concentration and $\delta^{18}{\rm O}$ analysis validated through multiple sulfate peaks, forest fires, the Tunguska explosion event, and a dust storm in 1842 reveal an average annual net accumulation of $\sim\!0.34$ at 46.25 m w.e. coincident with the depth of the Tambora eruption in 1815; 0.36 at 28.5 m w.e. coincident with the 1908 Tunguska explosion event, and $\sim\!0.35$ m w.e. in the upper 14.1 m w.e. coincident with the 1963 nuclear detonation.

To verify the credibility of the developed time scale (Table 1) a profile of annual accumulation rate from surface to 145 m w.e. was estimated for 1 m w.e. resolution (Fig. 7f) and for the main time-marked events (Table 1; Fig. 7g) using the modeled thinning coefficients. The last section of 0.865 m w.e. from the bedrock was excluded due to the nonlinear increase of modeled thinning coefficients.

Estimated annual accumulation rate varied on average from 0.16 m w.e. during cold periods, up to 0.70 m w.e. during warm periods of Altai's glaciation history (Figs 7f and g), demonstrating the credibility of the developed icecore time scale.

7. RESULTS

7.1. Ice-core depth/age scale and historical events

7.1.1. Younger Dryas

7.1.1.1. Intense depletion in δ^{18} O. It was observed in more than 100 ice-core samples (0.02–0.03 m w.e. resolution) at the bottom of the core, close to the bedrock (Figs 4 and 6a). The depletion in δ^{18} O from -10.8 to -21.3% indicates an extreme decrease in air temperature.

Taking into account the 14 C measurement at 145.117 ± 0.12 m w.e. depth dating to 9075 ± 1221 cal a BC (Fig. 5a (1); Section 3.2), modeled depth dating to 10411 a BC (Table 3) and validated dating through the highest maxima in non-dust sulfate fraction at 145.23 m w.e. depth, associated with the massive caldera-forming Khangar, Kamchatka eruption dated to 9500 ± 300 a BC (Siebert and Simkin, 2002) (Table 1), we assigned the 145.117 ± 0.12 m w.e. depth to 9700 cal a BC and the 145.23 m depth to 9800 cal a BC using the possible range of uncertainties in dating for both the 14 C estimation and the Khangar eruption (Table 3). Dating of these two horizons is in accordance with model-based dating, i.e. the discrepancy is within the uncertainty of measurements. The rest of the 0.64 m w.e.

to the bottom is related to the beginning of a significant drop in isotopes (Figs 5a(1) and 4a). We suggest this indicates the beginning of the YD in the Siberian Altai. The linear extrapolation to the bottom from 145.23 m locates the beginning of the YD at 10 950 cal a BC at 145.75 m w.e., approximately coinciding with the beginning of the GISP-2 YD event (Fig. 9a) (Peteet, 1995; Alley and others, 2000; Rasmussen and others, 2006; Lowe and others, 2008; Steffensen and others, 2008). The flow model (Fig. 7c, Table 3) suggests accelerated and unrealistic thinning of layers deeper than 145.23 m w.e., i.e. 32 585 cal a BC at 145.75 m w.e. and the basal ice at the bedrock of 145.865 m w.e. depth is dated at 303 070 years BC according to the model.

We suggest that the Altai's glaciers were re-generated during the YD. This is in accordance with radiocarbon measurements of organic soil from the bottom of a 87.46 m surface to bedrock ice core from the inner Tien Shan (Grigor'eva ice cap, Gr2007; 42°N, 78°E; 4563 m a.s.l.), about 1500 km southwest of the Altai. The radiocarbon measurements revealed that the present Tien Shan ice cap contains no ice that formed in the last glacial maximum (Fig. 9a) (Takeuchi and others, 2014).

The YD was identified in Northern Europe as a cooling event experienced throughout the entire North Atlantic Region. The end of the YD, based mainly on the GISP2 ice core, is 9640 a BC (Fig. 9a; Alley and others, 2000). In arid Northeast Asia, the YD was an exceptionally cool, dry climate dated between 10 900 and 9600 cal a BC (Herzschuh, 2006). However, this was not universally the case; ambiguities exist in the paleo-environmental record of the region, e.g. some lake basins along the eastern face of the Altai Mountains began to recover ~8000 cal a BC, and permafrost layers of Gobi Desert soils degraded ~8000 cal a BC as temperatures increased (Rhodes and others, 1996; Yang and others, 2004; Okishev, 2011).

Our results do not prove that the YD was synchronously recorded in the Altai and in Greenland. The deepest ¹⁴C measured horizon at 145.2 m w.e. depth in the Bl2003 ice core corresponds to 9075 ± 1221 cal a BC and assigned to 9700 cal a BC is located at the beginning of intensive depletion in δ^{18} O, while the same spot with age of 9700 cal a BC in the Guliya ice core (Thompson and others, 1997) and in the GISP2 (Alley and others, 2000) ice core corresponds respectively to the middle and to the end of isotope depletion (Fig. 9a). The second from the bottom ¹⁴C measured horizon at 142.82 m w.e. corresponding to 6197 ± 473 cal a BC and assigned to 6000 cal a BC, is located 0.45 m w.e. from the abrupt enrichment in isotopes at 143.27 m w.e., which was assigned to 6400 cal a BC (Table 1). The 1.8 m w.e. horizons between 145.2 and 143.4 m w.e. were significantly depleted. Two ¹⁴C dates (Figs 4d, 5a and 9a) at the bottom of the Bl2003 ice core, along with strong δ^{18} O isotope depletion and flow model dating suggest that the late glacial oscillation recorded in the Bl2003 ice core may be associated with the YD and it might have begun simultaneously with Greenland ice core records, but it was prolonged by more than millennium.

7.1.1.2. Significantly increased major ion concentrations. Up to 50 times for Na^+ (background), up to 45 times (background) for Ca^{2+} and Mg^{2+} , up to 20 times for SO_4^{2-} (background) relative to subsequent periods are observed at the beginning and end of the most intensive depletion of isotopes, which occurred during the YD (Fig. 6).

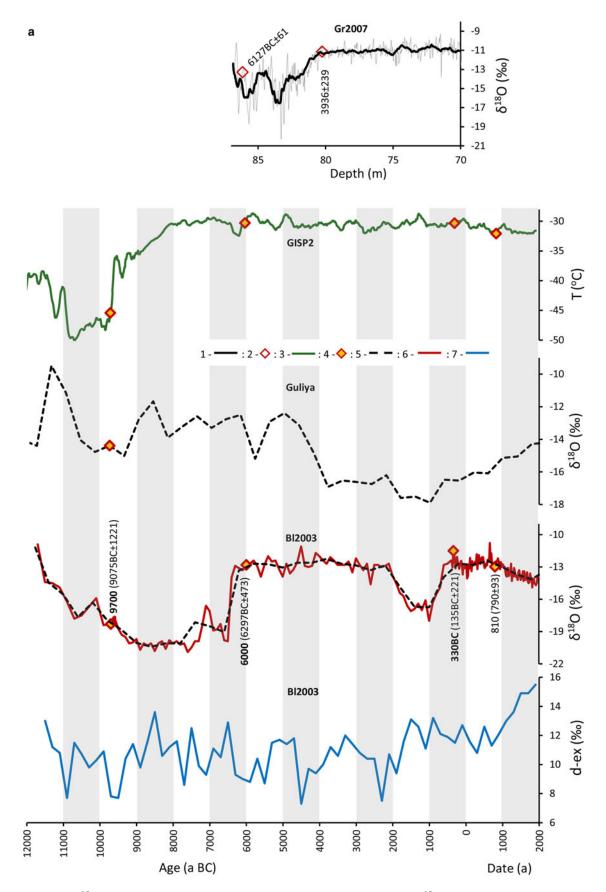


Fig. 9. Comparison of δ^{18} O and d-ex records from the Altai, Bl2003 (to bedrock) ice core with δ^{18} O records from inner Tien Shan, Grigor'eva ice core, Gr2007 (to bedrock, not dated) (Takeuchi and others, 2014), from Western Kunlun Shan, Guliya ice core (to bedrock) (Thompson and others, 1997) and from Altai, East Belukha ice core, Bl2001 (not to bedrock) (Henderson and others, 2006); with reconstructed mean air temperatures, T (°C), from Greenland GISP2 (Alley, 2000), GISP2' (Kobashi and others, 2011), and from the Barnaul meteorological station, with air temperature deviations, ΔT (°C), from Greenland GISP2" (Vinther and others, 2009) and with summer air temperature deviations, ΔT (°C), reconstructed based on ring-width chronology from Siberia, Yamal, (Hantemirov and Shiyatov, 2002) for the last (a) 13 700 years; (b) 2400 years of bi-decadal records and (c) 2000 years of decadal records. 1 is 15-record moving averages of δ^{18} O; 2 is δ^{14} C measured age for Gr2007; 3 and 6 are reconstructed air temperature, δ^{18} O and corresponding age (a BC, Date (a)); 4 is δ^{14} C measured age for Bl2003; 5 is four-centennial averages of δ^{18} O for Guliya and Bl2003; 7 is bi-centennial averages of d-ex records from Bl2003.

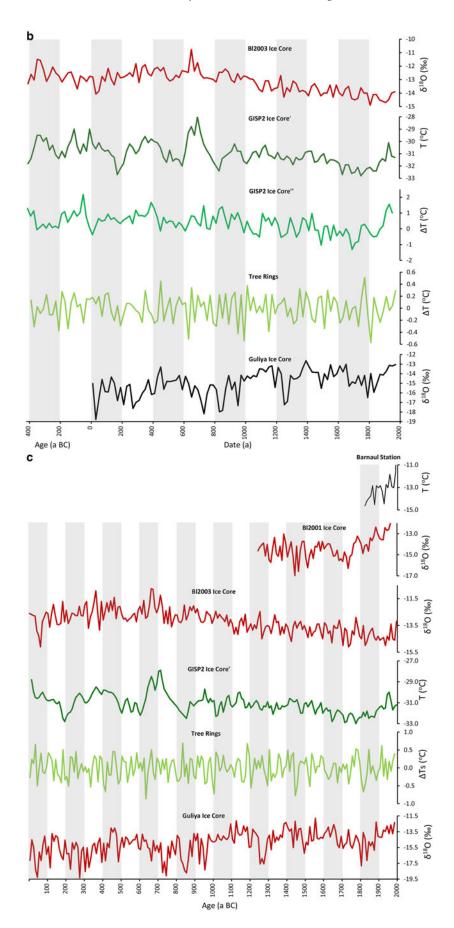


Fig. 9. (continued)

The ion concentrations reveal variable magnitude and distribution during the YD in K^+ and NO_3^- relative to maxima of $Ca^{2+},\ Mg^{2+},\ Na^+,\ Cl^-$ and $SO_4^{2-},\ pointing to different origin/causes of these two groups of ions/aerosols. A maximum in <math display="inline">K^+$ is not as significant as for $Ca^{2+},\ Mg^{2+},\ Na^+,\ Cl^-$ and SO_4^{2-} during the warm to cold transition period and is delayed during the cold to warm transition period of the YD. There is no obvious maximum in NO_3^- during the warm to cold transition period of the YD.

During the YD, the transition from warm to cold and vice versa led to steepening pressure gradients, enhanced wind intensity and numerous dust storms with associated increases in Ca²⁺, Mg²⁺, Na⁺, Cl⁻ and SO₄²⁻ concentrations. During the time of the most depleted isotope values, i.e. a period of minimum air temperatures, major ion concentrations (aerosol loading) decrease relative to the transition time from warm to cold and from cold to warm.

7.1.1.3. Air temperature and d-ex values. Average air temperature was 6 °C, reaching up to 9.0 ± 2.7 °C, lower during the YD compared with the recent period (Figs 8a and b). The Bl2003 ice-core stable isotope profile exhibits the lowest air temperature during the YD with a possible deviation of -12 °C relative to the recent period. During the YD average d-ex values ranged from 10.2 to 12.6% (Fig. 6b). These values are comparable with those for the Global Meteoric Water Line.

7.1.2. Pre Boreal (PB) and Holocene Climate Optimum (HCO)

7.1.2.1. δ^{18} O enrichment. The first short and abrupt warming event (AWE1), associated with δ^{18} O enrichment from -21.3 to -16.6% was dated at \sim 7300 cal a BC, preceding the cool, Pre Boreal Oscillation event (PBO), \sim 6900–6600 cal a BC (Fig. 5a(1); Table 1). Another warm period follows the large abrupt enrichment in δ^{18} O from -20.3 to -13.4% indicative of the HCO (Figs 5a(1) and 6). The most intensive enrichment of -10.5% occurred during the HCO, pointing to an increase in air temperature at \sim 5100–4600 cal a BC. The Bl2003 ice-core records revealed that the HCO lasted from \sim 6500 to 3600 cal a BC over Siberia.

A short depletion in δ^{18} O stable isotopes from -12.3 to -14.7% (Figs 4 and 5) with a 14 C radiocarbon date of 6297 \pm 473 cal a BC reveals a period with decreased air temperature referred to as the 8.2 ka sudden cooling episode. The cold phase \sim 6200 a BC was lasted by about 200 years across low- to mid-latitude regions (Zoller, 1960; Alley and others, 1997; Alley and Ágústsdóttir, 2005). However, the δ^{18} O signal from Bl2003 ice core as well as from Guliya ice core at the 8.2 ka cooling episode was not as pronounced as in Greenland ice-core records (Figs 5a(1) and 9a).

7.1.2.2. Major ion. Sharp decreases in major ion concentrations are observed at the end of transition time of sharp isotope enrichment (Fig. 6). A delayed maximum in K^+ and NO_3^- (relative to maximum in Ca^{2+} , Mg^{2+} , Na^+ , Cl^- and SO_4^{2-}) occurs during the large abrupt first warm events, AWE1, ~7400 cal a BC, after the YD.

During the HCO, under the intensive δ^{18} O enrichment, major ion content continued to drop reaching the lowest content $\sim 3000 \pm 200$ cal a BC after period before the severe centennial drought (SCD). Relative to YD the

declining ion content, up to 30 times for Na^+ (maximum), from 10 times for Ca^{2+} and Mg^{2+} , up to 15 times for SO_4^{2-} and just 2–3 times for K^+ and NO_3^- are observed after of the most intensive enrichment of isotopes.

7.1.2.3. Air temperature and d-ex values. According to geomorphologic analysis (Koshkarova and Koshkarov, 2004) in north-central Siberia, the HCO warm event consisted of a winter warming of 3-9 °C and a summer warming of 2-6 °C compared with the modern period. The Altai ice-core mean records reveal a large temperature difference of ~7 °C between the YD and HCO and ~5 °C between the HCO and the SCD (Fig. 8). During the Holocene Thermal Maximum, bicentennial means reached the maximum positive deviation, exceeding on average, 1.5 ± 2.7 °C relative to recent times, and 2.0 ± 2.7 °C relative to the modern period (Fig. 8b). During the warmest periods of the HCO with the highest bicentennial δ^{18} O mean (-10.53%) d-ex values drop to their lowest values and the bicentennial dex mean values reach a minimum of 6.1% (Fig. 9a).

7.1.3. Severe centennial drought

7.1.3.1. δ^{18} O depletion. The Bl2003 ice-core record reveals significant and prolonged depletion in isotopes from ~2000 to ~600 cal a BC (Figs 4, 5a(1), 6a and 9a; Table 1), concurrent with periods of SCD observed in North Africa, SE. Asia and N. America from 2400 to 1800 years BC (Claussen and others, 1999; Booth and others, 2005; Arz and others, 2006; Davis and Thompson, 2006; Parker and others, 2006; Menounos and others, 2008; Chun and others, 2011). The dating of the SCD corresponds with prolonged depletion in Guliya ice-core stable isotope records (Thompson and others, 1997). However, the SCD event was not pronounced in the GISP2 ice-core signal (Fig. 9a).

7.1.3.2. Major ions. Elevated ion concentrations (relative to their declines in the HCO) up to 5 times for Na $^+$, Cl $^-$ and SO $_4^{2-}$, 2 $^-$ 3 times for Ca $^{2+}$ Mg $^{2+}$, NO $_3^-$ and K $^+$ are observed at the beginning of the SCD during the second period of intensive isotope depletion, i.e. during the sharp transition from warm to cold conditions in the SCD. After this maximum, the major ion contents moderately and slowly decreased to pre-industrial low levels and have insignificant variability. There is no maximum in ion content at the end of SCD during the transition from cold to warm conditions as was observed during the YD.

7.1.3.3. Air temperature and d-ex values. Air temperatures declines a second time after the YD, down 5 $^{\circ}$ C from the HCO, however, not reaching the YD minimum of \sim 1.5 $^{\circ}$ C. Air temperatures are about \sim 3.5 $^{\circ}$ C lower than modern values (Fig. 8). D-ex values began to increase from about the time of the SCD lowest temperatures and reach their modern values, exceeding 14‰ (Fig. 6).

7.1.4. Medieval Warm Period (MWP) during Prolonged Warm Period (PWP)

7.1.4.1. δ^{18} O. The enrichment in δ^{18} O, from -19.4 to -10.1%, after the SCD (Fig. 4) ~600 cal a BC lasted until ~1100 AD, revealing a warm period, which includes the MWP, which began from 640 AD (Figs 5a(2,3), 6a, 9a and b). The corresponding 14 C date is 790 AD ± 93 consistent with flow model dating and peaks in volcanic eruptions

(Table 1). The most intensive enrichment in δ^{18} O (up to -8.9%) in the Bl2003 ice-core record occurred \sim 660 to 680 AD with a dating discrepancy of 5% (Table 3).

After isotope ratios enriched to the Medieval Thermal Maximum values, further cooling followed gradually with periods of more or less depleted isotopes. There is an observed negative trend in bidecadal isotope means since the Medieval Thermal Maximum (Figs 9b and 6a).

The end of the MWP in the Bl2003 ice-core record was associated with the beginning of a mild and continuous depletion in isotopes ~1100 AD, which is in accordance with the end of the MWP estimated by Briffa and others (1990), Mackay and others (2005) and Mann and others (2009).

Comparison of bidecadal mean stable isotope ratios revealed similar distributions in the Bl2003 and GISP2 icecore records (Kobashi and others, 2011) from 400 cal a BC to 1820 AD especially for the MWP. Analysis of a tree ring chronology also revealed an increase in reconstructed summer air temperatures (Hantemirov and Shiyatov, 2002) during the Medieval Thermal Maximum (Fig. 9b).

7.1.4.2. Major ions (Fig. 6). After the elevated ion concentration during the SCD, their content decreased with moderate variability and did not significantly change till the industrial period (IP).

7.1.4.3. Air temperature and d-ex values. During the MWP as well as in the HCO, air temperature was higher, on average \sim 1.5 °C, relative to the recent and modern warm period (MoWP) (Fig. 8). D-ex values fluctuated on average between 10 and 14‰ (Figs 6 and 9a).

7.1.5. Little Ice Age

7.1.5.1. δ^{18} O. The LIA appears to span the period 1400 to 1870 AD according to GISP2 chemical records in Europe (Mayewski and others, 1993; Meese and others, 1997; Bradley, 2000) and from ~1500 AD in China (Li and Ku, 2002), which experienced lower temperatures compared with the 20th century. There are several minima with warming intervals during the LIA (Mayewski and others, 1993; Meese and others, 1997). In Siberia, the LIA lasted from 1480 until 1880 AD based on data from sediments in the Teletskoe Lake (Butvilovskii, 1993; Panyushkina and others, 2000; Andreev and others, 2007).

The mild, continuous depletion in the middle part of the Bl2003 ice core, around the middle of the 15th century, is considered as the LIA (Figs 6a and 9c). The LIA is not obviously pronounced in the Altai Bl2003 ice-core isotope records. Depleted isotopes during the middle of the 15th century were followed by relatively enriched isotope values until the end of the 15th century. Following this, isotope depletion occurred near the turn of each century, lasting until the middle of the 20th century (Figs 6a and 9c).

7.1.5.2. Ion concentration. It was relatively low with periods of greater or lesser concentration. The end of the 15th/beginning of 16th centuries and the end of 19th/beginning of the 20th centuries are characterized by low concentrations of major ions. This was accompanied by the most depleted isotope content during the LIA, i.e. low temperatures (Fig. 6).

7.1.5.3. Air temperature. At the beginning of the 15th century, the climate was on average, 2 °C cooler compared

with the recent period based on the Bl2003 ice-core data (Fig. 8).

7.1.6. PI and IPs including modern and recent

7.1.6.1. δ^{18} O. During the MoWP from 1973 to 2003, a shift in climate appears marked by an observed enrichment in stable isotope values. However, the most enriched records are in the upper part of the Bl2003 ice core, up to -9.8%. Enrichment of stable isotope values in the Bl2003 ice core increases significantly from the beginning of the 1990s, i.e. during the recent warm period (ReWP) from 1993 to 2003 (Figs 5b and 6a). These values were not exceeded by any of those observed for the last 1000–1500 years. An exception is a short period with several enriched records, up to -9.0%, at the middle of the 18th century (Figs 5b(3) and 9c).

At the beginning of glacier generation (or regeneration), isotope records were more enriched than during the 30 years MoWP and then during the 10 years ReWP (means for: MoWP is $\delta^{18}O_{1973-2003} = -14.1\%$ and for ReWP: $\delta^{18}O_{1973-1993} = -13.3\%$; Table 2). At the bottom of the Bl2003 ice core, from 145.865 to 145.75 m w.e. depth several isotopically enriched records of up to -10.9% were revealed. During the HCO and MWP centennial mean isotope values are even higher, by up to -8.9%, than the 30 years MoWP and the 10 years ReWP means (Fig. 9a).

7.1.6.2. Major ions. Elevated sulfate and nitrate levels in the upper 17.8 m w.e. of the core are related to the Industrialization (IP) as of the early1950s, marked by an increasing trend ($p \le 0.001$, *F*-stat result using log-transformed concentrations) (Olivier and others, 2006; Joswiak, 2008) (Figs 6g and f). Despite the positive trend in the sulfate/ nitrate time series since the early 1950s, a decrease in concentrations occurred in the early 1990s during the ReWP reflecting a combination of several factors, including a short-run de-industrialization period subsequent to the dissolution of the Soviet Union in 1991, and global reduction of atmospheric sulfate in the early 1990s from decreased coal use and production (Stern, 2005). Low-level concentrations below 17.8 m w.e. provide insight into the PI background of atmospheric concentrations.

7.1.6.3. Air temperature and d-ex values. During the MoWP air temperature exceeded air temperatures during the YD, SCD, LIA and pre-IPs, it was about the same as during the beginning of IP, and lower by $1.0~^{\circ}$ C relative to HCO and the MWP. During the ReWP air temperature is lower by just $\sim 0.5~^{\circ}$ C than during the Holocene Thermal Maximum and the MWP (Figs 8a and b).

The d-ex values reach their maximum, on average significantly exceeding 14% and sometimes as high as 22% during the PI and IP till the end of 1970s. From the beginning of the 1980s when a sharp decrease in d-ex values is observed, d-ex values varied from 10 till 16%.

7.2. Comparison analysis of Bl2003 ice-core records with other paleo-climatic records

7.2.1. East Belukha ice core, Siberian Altai In July 2001, another ice core (Bl2001; not to bedrock) was obtained by a Swiss-Russian team from the saddle between the East and West Belukha peaks (49°48N, 86°34E; 4062 m a.s.l.) (Olivier and others, 2003, 2006; Henderson and others, 2006; Eichler and others, 2009, 2011) (Fig. 1c). The Bl2001 depth/age scale was derived for the 69.1 m w.e. core based on the 1963 peak in tritium and the record of ²¹⁰Pb radioactive decay since 1815 using modeled annual layer thinning (Haefeli, 1961). The average annual accumulation was reported as 0.560 m w.e. (Olivier and others, 2003), from the surface to 69.1 m w.e. (reference horizon of Tambora eruption) covering the time period, 1815–2001.

A lower accumulation rate was obtained from the West Belukha Plateau surface to bedrock ice core, Bl2003 (i.e. 0.34 m w.e. for the period, 1815–2001) in comparison with that reported by Olivier and others (2003). Accumulation differences are likely the result of variability in wind/snow redistribution caused by local orographic effects created by the two-steep slopes of the West and East Belukha peaks on the saddle where the Bl2001 was drilled, while the Bl2003 ice core was obtained from an open plateau (Figs 1b and c).

Marked events including the Mt. Pinatubo eruption in 1991, nuclear detonation maximum in 1963, the Novarupta eruption in 1912, the Tunguska event in 1908, the Mt. Krakatoa eruption in 1883, major dust storms in 1842 and the Tambora eruption in 1815, among others (Table 1) are preserved in both cores validating the depth/age scale developed for the Bl2003 core.

Decadal means of stable isotope ratios from the Bl2001 core were developed for the period, 1250–1980 (Eichler and others, 2009), (Fig. 9c). Estimated uncertainty of the Bl2001 core dating increases from <1 year at the δ^3 H peak to \sim 6 years at 1940, and to \sim 25 years at 1815 (Olivier and others, 2004), i.e. for the period covered by radioactive decay of 210 Pb. Discrepancies in dating the Bl2003 icecore records by different techniques is also \sim 1 year at the 1963 depth and 7–9 years at the 1815 depth (Table 3).

Comparison of the decadal mean stable isotope ratios revealed similar distributions in the Bl2001 and Bl2003 icecore records from 1250 to 1850 (Fig. 9c). The discrepancy in the distribution of the high and low values in the decadal means is within the uncertainty/discrepancy in dating the Bl2001 core (25 years at 1815; Olivier and others, 2004) and the Bl2003 core (7-9 years at 1815; Table 3). The variability in decadal means of δ^{18} O values obtained from the Bl2001 and Bl2003 ice cores is about the same ($\sigma = 1.0$ and 0.6%). Reconstructed November– May air temperature from the Bl2001 ice-core stable isotope records is based on data from Barnaul meteorological station (Eichler and others, 2009). Eichler and others (2009) found a δ^{18} O/air temperature slope of (0.88 ± 0.36) ‰ °C⁻¹ for decadal means in May-November monthly air temperature; our analysis revealed an air temperature/ δ^{18} O slope of (0.9 ± 0.08) °C $\%^{-1}$ (Eqn (6)). The slope in the inverse relationship between δ^{18} O/ air temperature is (1.1 ± 0.08) % °C⁻¹. Thus, both air temperature reconstruction techniques reveal slopes within the uncertainty in the δ^{18} O-surface air temperature regression.

From the middle of the 18th century, stable isotope records from the Bl2001 ice core reveal significant enrichment until the 1980s. Stable isotope records from the Bl2003 ice core do not reveal a significant enrichment trend until the middle of the 20th century, with the most significant enrichment from the end of the 1980s to the beginning of the 1990s (Figs 6a and 9c). The distribution of stable isotopes from the Bl2003 ice-core records is in

accordance with air temperature reconstructions from Okamoto and others (2011), which are based on stratigraphic analysis of the Bl2003 ice core.

The difference in decadal means of δ^{18} O is explained by the more significant fraction of radiation melt and partial percolation in Bl2001 at the upper part of the Bl2001 core (Henderson and others, 2006). Significant association between thicknesses of radiation crust in annual layers in Bl2001 and reconstructed air temperatures (Eichler and others, 2009) supports our explanation that the effect of solar radiation on snow melt and consequent stable isotopes is more significant at the Bl2001 drilling site than at the Bl2003 site. A decreased fraction of radiation melt at the insignificantly higher elevated Bl2003 drill site is likely responsible for the more depleted mean stable isotope ratio since the middle of the 18th century. The difference in radiation melt between the Bl2001 and Bl2003 drilling sites might be caused by differences in topography. Bl2001 is located on the saddle of a narrow field between the Belukha and West Belukha peaks (Fig. 1). Radiation melt and percentage of percolation with consequent freezing is more intense at B12001 than at Bl2003 because of multiple reflections of shortwave radiation from surrounding slopes covered by snow with high albedo, which significantly increases the diffuse and total radiation, especially under intense cloudiness. With the water phase change, isotopic fractionation enriches stable isotopes by 2-3‰ in the solid phase (e.g. O'Neill, 1968; Arnason, 1969; Nakawo and others, 1993).

Different wind/snow redistributions at the two drill sites could also cause the difference in decadal means of δ^{18} O. Higher snow accumulation at Bl2001 than at Bl2003 is a result of snow redistributed from nearby slopes. The additional snow brought from surrounding slopes at Bl2001 generally accumulated during the warm season (when the precipitation maximum occurs), increasing the decadal stable isotope means.

7.2.2. Greenland, GISP2 (Alley, 2000; Vinther and others, 2009; Kobashi and others, 2011); Western Kunlun Shan, Guliya (Thompson and others, 1997), Inner Tien Shan, Grigor'eva (Takeuchi and others, 2014) ice cores and northwestern Siberia, ring-width chronology (Hantemirov and Shiyatov, 2002) (Fig. 9) 7.2.2.1. YD and 8.2 ka event. Analysis of stable isotopes from the three surface to bedrock ice cores from different parts of central Asia and Greenland (Guliya, Bl2003 and GISP2) reveal the YD. The exception is Gr2007, where the ¹⁴C radiocarbon measurements from the surface to bedrock reveal the existence of grass during the YD (Takeuchi and others, 2014). The duration and intensity of this cool period differs geographically. The most intense drop and following abrupt rise in air temperature occurred over Greenland (Fig. 9a; Alley, 2000). The air temperature change was ~10 °C, while in the West Siberia, air temperature changed ~7–8 °C (sum of negative and positive deviations; Fig. 8b) and the depletion in isotopes was ~9%. The Guliya ice core demonstrates a weak depletion ~4-5‰.

The 14 C radiocarbon measured layer at the bottom of the Bl2003 ice core, of (9075 ± 1221) cal a BC assigned as 9700 cal a BC is the beginning of isotope depletion in the Bl2003 ice core, while the (9075 ± 1221) cal a BC in the GISP2 ice core corresponds to the end of the cool period of the YD in Greenland and to the middle part of the YD cool period in

the Western Kunlun, Guliya (Fig. 9a). The Western Siberia, Altai, had the most prolonged cool period of YD. In the Western Kunlun Shan, enrichment of isotopes after the YD cool period was not so intensive as in GISP2 or Bl2003. The depletion of isotopes/air temperatures over 8.2 ka is observed in all four surface-to-bottom cores, including Gr2000.

7.2.2.2. SCD. The Guliya and Bl2003 records contain a prolonged period in isotope depletion of approximately the same intensity (i.e. from 12 to 18‰) during the SCD, which is not pronounced in GISP2 records. The Guliya ice core shows an earlier time for the beginning of gradual isotopes depletion than the Bl2003 core, but the same period for the most intense depletion during the SCD (Fig. 9a).

7.2.2.3. The last 2400 years (MWP, LIA, PIP, IP, MoWP, RWP). For the last 2400 years, the distribution of bidecadal/decadal means in the Bl2003 stable isotope is in the best accordance with bidecadal/decadal means of reconstructed air temperature from GISP2 (Vinther and others, 2009; Kobashi and others, 2011) (Figs 9b and c). The correlation reaches 0.53 with data developed by Kobashi and others (2011) or 0.40 with data developed by Vinther and others (2009). The MWP is pronounced in both sets of data with a maximum in air temperature/ δ^{18} O ratio at ~640–700 AD.

There is a discrepancy between Bl2003 and GISP2 around the 20th century when reconstructed data from GISP2 shows an increase in air temperatures from the end of 19th to the beginning of 20th century, i.e. the end of the LIA, while the Bl2003 ice-core records demonstrate enrichment in isotopes from the middle of 20th century (Figs 9c and b).

Bidecadal/decadal means in stable isotope records from the Guliya ice core (Thompson and others, 1997) do not show a significant correlation with corresponding Bl2003 ice-core records for the last 2000 years, however there are similar periods in δ^{18} O enrichment (e.g. ~440, 980, 1660) and depletion (e.g. ~40 AD, 1200, 1260, 1500, 1810) in both cores (Fig. 9c). Summer air temperature deviations reconstructed from the tree ring chronology (Hantemirov and Shiyatov, 2002) are similar in distribution to Bl2003 δ^{18} O records, with periods of isotope enrichment/high summer temperatures (e.g. ~130, 450, 660, 980, 1180, 1660, 1830) and depletion/low summer temperatures (e.g. ~40, 530, 640, 1110, 1200, 1380, 1730, 1810, 1920, 1940) (Fig. 9c). Neither Bl2003 ice core δ^{18} O records nor tree ring chronology from the northwest Siberia demonstrate air temperature growth from the end of 19th century.

8. DISCUSSION

8.1. The post-depositional processes

Temperature measured in the 171 m deep borehole suggests that West Belukha Plateau lies in the cold recrystallization zone, where any meltwater subsequently refreezes below the surface and there should not be ion diffusion in the Bl2003 ice core. Stratigraphic analysis of Bl2003 ice core indicates an absence of percolation. Analysis of the δ^{18} O/ δ D relationship in the Bl2003 ice core also indicates an absence of intensive melt and consequent percolation. The varied slopes the in δ^{18} O/ δ D relationship do not approach typical sublimation/evaporation slopes, suggesting it is unlikely that evaporative/sublimation changes occur at the

site. Snow/wind redistribution over the open West Belukha Plateau is just one of the post depositional processes that could insignificantly impact on ice-core records on the Belukha Plateau, most probably during winter. According to automatic twice-daily measured snow surface level, there is no sign of wind redistribution during the warm season till October (Aizen and others, 2005). Furthermore, according to stratigraphy analysis, no significant post-depositional effects were apparent in the records from the Bl2003 ice core, as stable isotope records from the surface to the 51 m w.e. yield well-preserved seasonal signals of δ^{18} O.

8.2. The YD event

The YD event recorded in the Bl2003 core likely began simultaneously with the YD in Greenland ice-core records, but it was more prolonged. Our results of the prolonged YD dating through Bl2003 ice-core records are in accordance with Rhodes and others (1996), Yang and others (2004), and Okishev (2011) results. Furthermore, according to Saarnisto (2000) the maximum extent of western Siberian glaciation during the LGM as well as the YD was reached one millennium later than the extent of maximum glaciation in Europe.

According to Steffensen's and others (2008) results, the precipitation moisture source of Greenland switched within 1-3 years over the YD transition and initiated an abrupt change of the Greenland air temperature. Steffensen and others (2008) suggest that a northern shift of the Intertropical Convergence Zone could be the trigger of these abrupt shifts of Northern Hemisphere atmospheric circulation. We assume that the changes in YD air temperatures recorded in the Bl2003 ice core were also caused by changes in atmospheric circulation/pressure, with consequent changes in sources of moisture, wind speed and in atmospheric dust loading from expanded Asian deserts (Kazakh steps, Muyun Kum, Gobi and Taklamakhan). Dust, which could explain the prolonged YD event, was intensively eluted and accumulated in Asian deserts after the LGM when Siberian and Central Asian glaciers melted. The transition from warm to cold and vice versa led to steepening pressure gradients resulting in enhanced wind and frequent dust storms with associated increases in Ca²⁺, Mg²⁺, Na⁺, Cl⁻ and SO_4^{2-} concentrations. During the time of the most depleted isotope values in YD (minimum air temperatures), major ion concentrations decreased, relative to the timing of changes in air temperatures, and intrusion of dust from Asian deserts to the Siberian Altai was not as intense as during the transitional time. During the minimum air temperatures of the YD, regional convective processes were reduced and mineral dust loading weakened.

Values of d-ex comparable with the Global Meteoric Water Line during the YD suggest that the western, northwestern and northern air masses originating over the Atlantic Ocean are primarily responsible for bringing precipitation to the Altai Mountains. This precipitation is not significantly modified by recycled moisture.

Uneven variability in K^+ and NO_3^- ions relative to Ca^{2+} , Mg^{2+} , Na^+ , Cl^- and SO_4^{2-} concentrations during the YD suggests their different origin. K^+ and NO_3^- are the most suitable biomass burning proxies (Eichler and others, 2011), while Ca^{2+} , Mg^{2+} , Na^+ , Cl^- and SO_4^{2-} are suitable as dust storm proxies for the Siberian Altai ice cores. A maximum in K^+ and NO_3^- occurs not during the YD, but during the large abrupt warm events after the YD. We assume there was

insufficient biomass available for burning during the time of the most depleted isotopes/lowest temperatures of the YD. The enriched isotopes associated with increased temperature during the AWE activated biomass growth with consequent burning under, most probably, dry and still windy conditions.

8.3. Holocene Climate Optimum

We suggest that during the HCO, high moisture availability in the Altai was associated with intrusions of Atlantic air masses as well as with moisture originating from the Pacific, evidenced by δ^{18} O and d-ex (Aizen and others, 2005, 2006) that maybe associated with the Eastern Asian Pacific summer monsoon. Continental recycled moisture was negligible, probably caused by high air humidity during one of the warmest periods in the Holocene. Combined paleo-evidence (Petit-Maire and others, 1994) suggests that the Eastern Asian monsoon penetrated more than 300 km northwestwards into Inner Mongolia between ~7500 BC and ~3000 BC exceeding its modern limit of extension. This agrees with Ricketts and others (2001) data from an ~8000 years record of hydrological change within Issyk Kul Lake (inner Tien Shan) based on sedimentary, faunal and geochemical evidence from piston cores, attributing high moisture availability in the early Holocene period to strengthening Asian and Indian summer monsoons. The sharp drop in ion content in the BL2003 ice-core records could be associated with increased precipitation during the HCO relative to the YD.

8.4. SCD, MWP and LIA

Water cycle changes in the Siberian Altai resulted in more cold and probably arid conditions from $\sim\!2000$ to 600 cal a BC yielding a transition to the SCD. The elevated concentrations of K⁺ and NO $_3^-$ during the beginning of the SCD cold period may be associated with sufficient biomass developed during the preceding wet and warm period of the HCO. The biomass burning was intensified during the subsequent dry SCD that resulted in increased K⁺ and NO $_3^-$ concentration in the Bl2003 core.

We suggest that the fraction of re-evaporated moisture from the Aral-Caspian endorheic basin began to increase during the SCD with a maximum fraction during the Pl. However, the Oceanic sources of moisture are still the prevalent sources during the SCD and MWP with insignificant fractions of continental (or recycled) moisture. The high values of d-ex, exceeding 14‰ during the LIA, are associated with an increased fraction of precipitation of inter-continental origin in the Altai.

8.5. PI and IP

During the ReWP air temperature almost reaches HCO and MWP high temperatures. The maximum values of d-ex during the PI and IPs, till the end of 1970s, suggest that intercontinental moisture was the main source of precipitation. We suggest that from the beginning of the 1980s oceanic moisture again became the prevalent source.

9. CONCLUSIONS

Radiocarbon analysis of the POC fraction, stable isotope records and derived temperature estimations from the Bl2003 ice core suggests that modern Altai glaciers were re-generated during the YD, when air temperatures in the Siberian Altai were, on average, \sim 6 °C lower than during the Recent Warming Period, and reveal an abrupt \sim 7 °C increase in air temperature after the end of the YD.

In addition, during the YD, Bl2003 major ion records exhibit the highest concentrations displayed in the entire ice-core record. Following the Younger Dryas, major ion concentrations decrease reaching the lowest mean levels during the modern/recent period. The exceptions to these trends are sulfate and nitrate, which begin to increase in concentration during the early 1950s, reflecting modern industrialization. Bl2003 results are in accord with analyses from Greenland (Mayewski and others, 1997; Taylor and others, 1997), Antarctica (Jouzel and others, 1996) and tropical alpine (Thompson and others, 1995) ice cores, which also show high concentrations of mineral dust during the YD cold period. Elevated major ion concentrations during the YD can be explained by the intercontinental location of the Altai Mountains and large mineral dust sources from Asian deserts.

The Bl2003 δ^{18} O signal, along with ¹⁴C radiocarbon measurements, reveals a period with decreased air temperature corresponding with the 8.2 ka sudden cooling episode. In addition, the Bl2003 ice-core records, as well as the Guliya ice-core records (Thompson and others, 1997) reveal the prolonged period in isotope depletion of approximately the same intensity from ~2000 to 600 a BC, which is associated with the Severe Continental Drought. During this period air temperatures, on average, were ~4.5 °C lower than during the Recent Warming Period.

The subsequent cold period from the middle of the 15th century until the middle of the 20th century was mild and was associated with the LIA, when air temperatures were, on average, ~2 °C lower than during the recent period in the Siberian Altai.

The Altai glaciers survived the AWEs of the Holocene Climatic Optimum, which lasted over Siberia from ~6500 to 3600 cal a BC, through the MWP (640-1100 AD) and MoWP (1973–2003). The most intense enrichment of δ^{18} O in the Bl2003 ice core is related to ~660 AD, the Medieval Thermal Optimum. The Modern Warm Period, 1973–2003, represents a shift in Altai climate marked by an observed increase in air temperature, a weakening in the intensity of the westerlies and increases in inputs of recycled moisture from intercontinental Asia, which severely impacts glaciological conditions in the Altai. Despite these recent significant changes, recent air temperatures (1993-2003) are, on average, 0.5 °C lower than air temperatures estimated during the MWP and Holocene Climate Optimum. During the current Altai's neo-glaciation existence, colder than modern periods occurred for ~6.5 ka during the Younger Dryas, PBO event and SCD, and periods warmer than modern periods occurred for ~6.5 ka including during the HCO and Medieval Warm Period.

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APPENDIX

CCI UM	Climate Change Institute at the University of
ISU	Maine, USA Idaho State University, Environmental
	Monitoring Laboratory, USA
NICL	National Ice Core Laboratory, USA
NIPR	National Institute for Polar Research, Japan
NU	Nagoya University, Japan
RIHN	Research Institute for Humanity and Nature,
	Japan
UI	University of Idaho, USA
Bl2003	ice core drilled to bedrock on the Western
	Belukha Plateau at 4115 m a.s.l. by US/
	Japanese team in 2003 (current research;
	Takeuchi and others, 2004; Aizen and
	others, 2005)
Bl2001	ice core (not to bedrock) drilled on the saddle
	between the east and west Belukha Peaks at
	4062 m a.s.l. by Swiss team in 2001 (Olivier
	and others, 2003)
GISP-2	ice core records from Greenland Ice Sheet
	Project Two (Alley, 2000; Kobashi and
	others, 2011; Vinther and others, 2009)
¹⁴ C	radiocarbon records
$\delta^{18}O/\delta D$	stable isotopes records
³ H	radiogenic measurements of tritium
	concentration

AWE1 concentration first short and abrupt warming event

BA Bølling- Allerød period HCO Holocene Climate Optimum

IP Industrial Period
LGM Last Glacial Maximum

LIA Little Ice Age

MoWP Modern Warm Period MWP Medieval Warm Period

PB Pre Boreal

PBO Pre Boreal Oscillation event

PI Pre-Industrial Period

PWP Pre-Medieval Warm Period ReWP Recent Warm Period SCD severe centennial drought

SH Siberian High YD Younger Dryas

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