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Geochemical evidence of the presence of volcanic and meteoritic materials in Late Pleistocene lake sediments of Lithuania

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ABSTRACT

Concentrations of trace elements in four Late Pleistocene lake sediment sequences across Lithuania were studied using inductively coupled plasma-mass spectrometry (ICP-MS). Such elements as Cr, Cu, Eu, La, Ni, Zn, Zr, and platinum group elements were used for constraints. The studied sediments deposited during the time interval from Bølling to Allerød and to Younger Dryas. Material for sediments of the Dengtiltis and Krokšlys sequences was delivered from the same or very similar source. Geochemical features of the sediments are consistent with the presence of extraterrestrial material in at least two horizons separated by ~2000 years, and resulted from two separate events. The younger horizon is detected in all studied sequences and corresponds to the age of ca. 11.0–11.5 ka BP. Its geochemical features are suggested to result from a local meteorite impact/bolide explosion tentatively related to the Velnio Duobės meteorite crater. The older horizon detected only for the Ūla-2 sequence corresponds to the age of ca. 13.5 ka BP and is due to the bolide airburst. There is also suggested meteoritic material in sediments dated as ca. 12.9 ka BP. The presence of volcanic materials related to the volcanic activity in the French Massif Central (a volcano of ca. 15.3 ka BP), and Laacher See volcano in Germany (12.88 ka BP) are suggested for some sedimentary layers of the studied sequences.

1. Introduction

In the Northern Hemisphere, the last glacial–interglacial transition ended with the beginning of the cold period known as the Younger Dryas (YD) climate oscillation, which occurred between 12.9 and 11.7 ka BP (e.g., Peteet, 1995; Alley, 2000; Björck, 2007; Lowe et al., 2008). This climate oscillation is generally thought to result from an abrupt change of atmospheric and oceanic circulation (e.g., Berger, 1990; Teller et al., 2002; McManus et al., 2004; Brauer et al., 2008; Murton et al., 2010). However, there are other hypotheses including such as that proposed by Firestone et al. (2007). This hypothesis suggests that just before the onset of the YD cooling (ca. 12.9–12.8 ka BP), a large bolide exploded over the North American Laurentide Ice Shield, and consequences of such a catastrophic event ("meteorite impact winter") led to a global climate change. Suggestions about both the extraterrestrial (ET) event itself and its influence on the Earth's climate resulted in a wide-spread discussion, which has yet to result in a decisive conclusion (see Pinter et al., 2011; Bunch et al., 2012; Israde-Alcántara et al., 2012; LeCompte et al., 2012; Wittke et al., 2013; Wu et al., 2013; van Hoesel et al., 2014 for details).

If the Late Pleistocene ET event occurred over North America, transportation of the related microparticles eastward by the dominating west winds (e.g., Isarin and Renssen, 1999; Brauer et al., 2008) could result in distal fallout from the impact/airburst cloud as far as Europe (cf. Bunch et al., 2008; Artemieva and Morgan, 2009). However, the studies of the YD impact hypothesis in Europe are so far very limited (e.g., Beets et al., 2008; Tian et al., 2010; Marshall et al., 2011; van Hoesel et al., 2012, 2014; Wu et al., 2013; Andronikov et al., 2014). In order to extend our knowledge about the possible presence of the ET material in the Late Pleistocene sediments of Europe, we conducted geochemical analyses of sediments in sequences from four localities in Lithuania (Fig. 1). This way, it is possible to decipher the trace element distribution across the sequences and to detect the presence of anomalous (in particular, ET-related) components.

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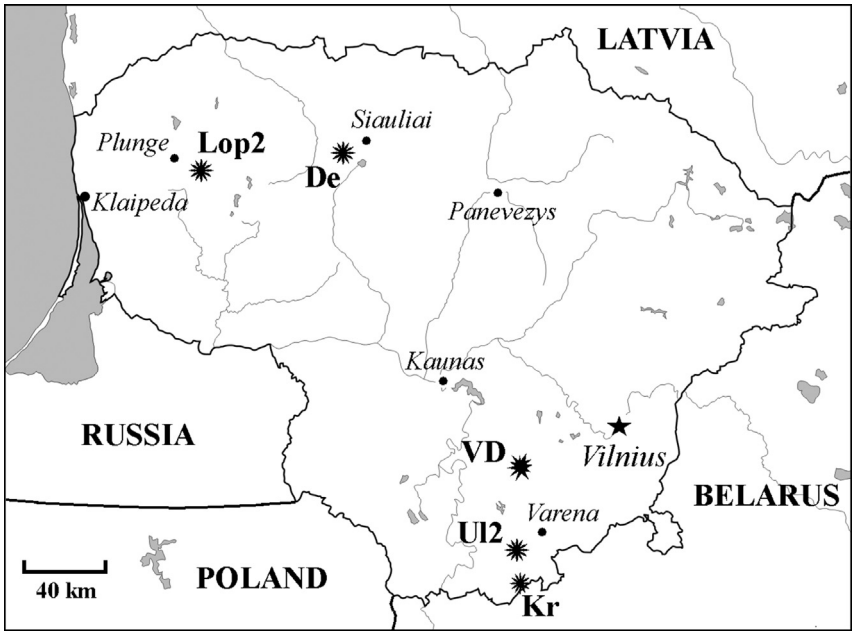

Fig. 1. A map showing the location of the studied sedimentary sequences in Lithuania (black asterisks). De, Dengtiltis outcrop; Lop2, Lopaičiai-2 drilling site; Kr, Krokšlys outcrop; Ul2, Ūla-2 outcrop; VD, Velnio Duobės structure.

2. Materials and methods

2.1. Study sites

Late Pleistocene lake sediments were collected from four sites across Lithuania: Dengtiltis outcrop located ~20 km SW of Šiauliai at N 55°46′16″ and E 23°07′08″ on an abrupt bend of Dubysa River; Lopaičiai-2 drilling site located ~30 km SE of Plungė at N 55°44′38″ and E 22°11′34″ in a little hollow on a hill of 210 m a.s.l.; Krokšlys outcrop located ~10 km SW from Varėna at N 54°02′31″ and E 22°37′58″ on the left bank of the Ūla River; and Ūla-2 outcrop located ~20 km SW from Varėna at N 54°06′34″ and E 24°28′44″, also on the left bank of the Ūla River (Fig. 1). Ūla is a river in Dzūkija National Park in southern Lithuania flowing across various aeolian relief forms.

The studied part of the Dengtiltis sequence (Fig. 2a) is lithologically homogeneous and represented by fine yellowish to brownish carbonaceous sand. The studied part of the Lopaičiai-2 sequence (Fig. 2b) is lithologically inhomogeneous and consists of three different parts: the lower to middle part of the section is represented by fine yellowish sand, the middle to upper part by dark-grey clay with thin interlayers of gyttja, and the uppermost part by peat. The studied part of the Krokšlys sequence (Fig. 2c) is also inhomogeneous and consists of yellowish sand at the lowermost studied levels, peat in the middle part of the section, and fine aeolian sand at the middle to uppermost levels. The studied part of the Ūla-2 sequence (Fig. 2d) is inhomogeneous, displaying yellowish (limonitized) sand at the lowermost studied levels, and gyttja with mollusk shells for the rest of the studied part of the sequence, which becomes silty clay at the uppermost levels.

2.2. Sample preparation and analytical techniques

A few grams of material from each sample were dried overnight at 105 °C and then pulverized in an agate mortar. Approximately 50 mg of the pulverized material from each sample were digested in a mixture of concentrated HNO_3 and HF in 15 ml Teflon beakers. The beakers were sealed and heated on a hot plate at 130 °C for 48 h during which time they were ultrasonicated twice. After cooling, this solution was dried down and then brought back to the solution with 5% HNO_3. Visual inspection revealed that the samples completely dissolved. The solutions yielded approximately 100 μg/ml of total dissolved solids for further analyses for most trace elements and 300 μg/ml for platinum group elements (PGE) because of general very low PGE concentrations in terrestrial sediments. For this pilot study, we needed only to recognize features of the PGE behavior in different samples. Therefore, we did not conduct PGE enrichment with the use of column chromatography, but instead analyzed the bulk samples as they are in order to compare PGE signal intensities from different samples on the ICP-MS spectra. For the PGE, we additionally analyzed aliquots of marls from Murray Springs, Arizona (USA), which are similar in concentrations to the Average Continental Crust (ACC; Wedepohl, 1995) (authors' unpublished data). Samples signal intensities were corrected to the sample mass and then normalized to the marls (≈ACC) intensity. Rhenium-185 was monitored as an internal standard during the PGE runs. The following isotopes were monitored during the analytical runs: P^{31}, Sc^{45}, Ti^{47}, V^{51}, Cr^{52}, Co^{59}, Ni^{60}, Cu^{63}, Zn^{66}, Rb^{85}, Sr^{87}, Sr^{88}, Y^{89}, Zr^{90}, Nb^{93}, Ru^{101}, Rh^{103}, Pd^{104}, Pd^{105}, Sn^{118}, Cs^{133}, Ba^{137}, La^{139}, Ce^{140}, Pr^{141}, Nd^{144}, Nd^{146}, Sm^{147}, Eu^{153}, Gd^{157}, Tb^{159}, Dy^{163}, Ho^{165}, Er^{166}, Tm^{169}, Yb^{172}, Lu^{175}, Hf^{178}, Ta^{181}, W^{182}, Re^{185}, Os^{189}, Os^{192}, Ir^{193}, Pt^{195}, Pb^{206}, Pb^{208}, Th^{232}, and U^{238}. Analyses were run in a low resolution mode for all isotopes and additionally in a medium resolution mode for P^{31}, Sc^{45}, Ti^{47}, V^{51}, Cr^{52}, Co^{59}, Ni^{60}, Cu^{63}, and Zn^{66}. An analytical blank solution was prepared using the same procedure. A Finnigan Element2 inductively coupled plasma-mass spectrometer (ICP-MS) was used for analysis. Solution standards consisted of known amounts of the analyzed elements and were prepared using multi-element solutions obtained from High-Purity Standards (Charleston, SC, USA). Sample concentrations were determined by first subtracting blank signal intensities from those obtained from the sample and standard solutions. A calibration curve was obtained by performing a linear least-squares regression for each element using the blank-subtracted counts and the known