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### ABSTRACT

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# Oxygen isotope compositions of conodonts – analytical challenges of *in situ* SIMS studies

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Reliable deep-time environmental and climate reconstructions are needed to understand the drivers of Earth's system evolution over geological time. Palaeozoic temperature estimates, including reconstructions of the climate change through the Ordovician, are based mainly on oxygen isotope ( $^{18}\text{O}/^{16}\text{O}$ ;  $\delta^{18}\text{O}_{\text{VSMOW}}$ ) thermometry derived from carbonate rocks with fossils such as calcitic brachiopods and phosphatic conodonts that are often the best preserved repositories of environmental conditions.

Palaeoenvironmental reconstructions are reliable only if the geochemical data is obtained using well-calibrated analytical tools. Most previous research devoted to oxygen isotope composition of conodonts has been conducted using the bulk method (gas source isotope ratio mass spectrometry (GS-IRMS)) that typically requires pooling several dozens of conodont elements for a single isotope ratio measurement. As such, studies of conodont-poor intervals and assessments of taxon-specific  $\delta^{18}\text{O}$  variability require extensive sample preparation and are challenging using the bulk method. Such challenges can be addressed by *in situ* secondary ion mass spectrometry (SIMS) analyses using only picogram sampling masses. However, several studies have reported inconsistencies between SIMS and GS-IRMS  $\delta^{18}\text{O}$  data for the same research material. We aim to solve this controversy by establishing a robust analytical protocol for conodont isotope analysis by SIMS.

Here we present conodont data on *Pterospathodus* and *Amorphognathus* specimens extracted from Ordovician strata in Nurme and Mehikoorma-421 boreholes (Estonia). Oxygen isotope composition of conodonts was analysed by both SIMS and GS-IRMS, where we paid particular attention to four inorganic apatite reference materials in order to understand the offset between these two techniques that have been reported in the literature. While the results of GS-IRMS measurements conducted using high-temperature reduction of  $\text{Ag}_3\text{PO}_4$  represent exclusively  $\delta^{18}\text{O}$  of phosphate-bound oxygen, SIMS analyses do not discriminate between different oxygen components (e.g.,  $(\text{PO}_4)^{3-}$ ,  $(\text{SiO}_4)^{4-}$ ,  $(\text{CO}_3)^{2-}$ , and  $(\text{OH})^-$ ) in apatite, inherently providing information on pooled isotope compositions. We conducted quantitative chemical analyses of selected conodont elements by electron probe microanalysis to assess to what extent matrix effects cause the offsets between the two isotope techniques. We also used scanning electron microscopy and white light optical profilometry to evaluate sample topography and porosity, which have a major impact on SIMS data quality.

We collected oxygen isotope data using a CAMECA 1280-HR large geometry instrument at the Potsdam SIMS user facility over several months to determine reproducibility of the results and to optimise a routine measurement protocol. Our tests included a variety of instrumental settings, e.g., different raster parameters for both pre-sputtering and data collection, which yielded slightly differing results due to different instrumental mass fractionation. SIMS is a comparative method, and as such relies on reference materials that have been previously characterised by bulk methods, ideally provided by multiple laboratories. We noted that the inconsistent offsets between SIMS and GS-IRMS data obtained for a given conodont specimen (with SIMS  $\delta^{18}\text{O}$  values in most cases being higher) are linked to reference material measurements that are necessary for conodont data calibration and are often biased towards lighter  $\delta^{18}\text{O}$  values. Our tests show that such bias is even more significant when calibration is based on a single reference material characterised by a single GS-IRMS laboratory, which has been a common practice in past conodont studies.