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Evaluation of the Role of Matrix Matching for LA-ICP-MS Calibration Approaches in Quantitative Elemental Analysis of Tooth Enamel

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Abstract. A mineral apatite –based calibration approach for Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) was proposed in this work to be used for quantitative multielemental analysis of tooth enamel samples. Tooth enamel is composed mainly of hydroxyapatite therefore natural apatite crystals were expected to fit the matrix. Mineral samples were partially digested and quantitatively analyzed in respect of their bulk, elemental composition by means of ICP-MS/OES. The obtained quantitative data were used to construct the LA-ICP-MS calibration curves based on the apatite crystals for the selected 32 elements. The correlation coefficient values were calculated for each element and varied from none correlation for the most heterogeneous element (Al) to the value above 0.99 (U, REE, etc.), while calibration curve based on 3 selected mineral samples was applied. The usefulness of the proposed calibration approach was evaluated during investigations of elemental composition of tooth enamel and reference materials (NIST 1400, NIST 1486) leading to the promising results.
Key words: LA-ICP-MS; matrix-matching; calibration.

Resumen. En este trabajo, se presenta un nuevo procedimiento de calibración para la cuantificación multi-elemental en esmalte de dientes por ablación láser y espectrometría de masas con ionización en plasma acoplado inductivamente (LA-ICP-MS); basado en el uso de apatitas minerales. Debido a que el esmalte dental está compuesto principalmente por hidroxiapatitas, para simular composición de muestra en la etapa de calibración, se utilizaron cristales de apatitas naturales. Estos minerales fueron parcialmente digeridos, determinando en cada uno de ellos la concentración de 32 elementos por espectrometría de emisión atómica con excitación en ICP (ICP-OES). Los resultados obtenidos para tres diferentes minerales se utilizaron para construir las curvas de calibración en el método LA-ICP-MS; obteniéndose los valores del coeficiente de correlación desde totalmente insatisfactorio para el elemento más heterogéneo (Al) hasta el valor superior a 0.99 para tierras raras (U, REE, etc.). La utilidad del procedimiento de calibración propuesto se demostró mediante el análisis de dos materiales de referencia certificados (NIST 1400, NIST 1486). Finalmente, se llevó a cabo la determinación de la composición elemental del esmalte dental, arrojando resultados prometedores.
Palabras clave: LA-ICP-MS, simulación de matriz; calibración.

Introduction

Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) is a powerful method for direct analysis of solids and allows for obtaining information on elemental composition with variable lateral or depth resolution and high sensitivity [1,2]. A number of substantive arguments support the use of LA-ICP-MS in geological [3-6] and biological investigations [7-9], such as tissue analysis, but on the other hand, there are also counter-arguments against it. One of the main restriction is the chemical diversity of samples, for which the matrix-matching of LA-ICP-MS analytical protocol can be very

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difficult. The use of suitable matrix-matched solid reference materials for calibration would increase the reliability of the final results [10,11].

The limited number of commercial matrix-matched reference materials promotes the use of various in-house standards. They are mainly used in the form of powders spiked with elements of interest before pressing to form a pellet. Mixing of powdered RMs with binding agents is an alternative way of their immobilization [12]. Nevertheless, these reference materials rarely reflect the physico-chemical properties of the analyzed materials, like density, hardness or absorption coefficient, which influence the interaction between laser and a sample. To overcome aforementioned limitation, matrix-matched natural minerals have been applied in quantitative analysis of titanites and sulfides [13,14]. The usefulness of natural materials and rocks as external standards can be observed in the number of commercially available certified reference materials produced from the geological samples. Sierra de Pachuca and Glass Buttes obsidians were applied in glass and obsidians provenance studies [15], while andesite (AGV2), granodiorite (GSP2) and rhyolite (RGM1) elaborated in U.S. Geological Survey were used in ceramic elemental analysis [16].

The majority of CRMs are silicates compounds; therefore, another challenge consists on very limited number of sulfide, carbonate and phosphate reference materials [17]. Bones are composed mainly of bio-apatites which are accompanied by different amount of organic substances, while tooth enamel is the most mineralized, and hard, calcified tissue [18]. Assuming similar chemical composition of enamel and natural apatite it was interesting to evaluate the possible use of well crystallized natural minerals as calibration standards for matrix-matched calibration approach for LA-ICP-MS elemental analysis.

Apatite is the most common representative of the phosphates group of minerals, it is also the one of few minerals which are produced and used by biological organisms. The basic formula of hydroxyapatite is $Ca_{10}(PO_4)_6(OH)_2$, but the hydroxyl groups (OH) can be replaced by fluoride, chloride or carbonate anion; phosphate groups can be replaced by carbonate, arsenate, silicate, vanadate or sulfate and the calcium cations may be replaced by magnesium, strontium, manganese, REE or other elements [19-21]. The P_2O_5 content in apatite (of igneous and metamorphic origin) can vary between ca. 37÷43 wt. %, whereas the CaO content varies between c.a. 52÷57 wt. % [20]. According to the literature, bones, teeth as well as sedimentary carbonate apatites contain only slightly less P_2O_5 (c.a. 35÷39 wt. %) and CaO (c.a. 46÷52 wt. %) [20,22]. Therefore, natural apatite crystals were expected to suit the matrix of tooth enamel better than SRM NIST 610 which is commonly used as the external standard during LA-ICP-MS investigations. It is also important to note, that natural apatite crystals are easily available and inexpensive. Large sets of crystals can be subjected to elemental analysis and only selected, the most homogeneous material can be used for the further investigations.

There are different calibration approaches described in the literature in the context of bone tissues analysis by means of LA-ICP-MS. Homogeneous NIST glass standards can be used without any additional pretreatment [23,24], while powdered matrix-matched in-house standards based on precipitated apatite [11,25] or Standard Reference Materials NIST 1400 (bone ash) and NIST 1486 (bone meal) [26] need pelletizing to allow execution of laser ablation. Both, NIST 1400 and NIST 1486, could be considered as the matrix matched reference materials but the interaction of laser energy with dense tooth enamel and the pressed pellets differs, therefore searching for a new calibration approach was still justified.

Fast screening of the bulk elemental composition of natural apatite crystals was proposed in this work to select the most appropriate crystals and construct the calibration curve based on the knowledge about their variable elemental composition. Johnstone et al. [26] reported the heterogeneity of elemental composition of natural apatite crystals while they were used during LA-ICP-MS determination of U and Th. Here, the use of natural apatite crystals may ensure tooth enamel matrix matching to construct multi-point calibration curves for over 30 elements. At the same time the certificate of NIST 1400 includes information about 17 elements, and NIST 1486 for 18 elements. The quantification of the obtained results for the Reference Materials (NIST 1400 and NIST 1486) and tooth enamel samples were compared for two approaches based either on the use of the non-matrix matched calibration utilizing NIST 610 as the external standard or on the proposed matrix-matched calibration.

Experimental

Geological samples

Five apatite crystals from various locations: unknown (A1); region of Baikal in Russia (A2 and A3); Atlas (A4 and A5) in Morocco were used in this study. Each of the selected crystals was cut into 2

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pieces and devoted to the parallel, independent measurements either by direct LA-ICP-MS or by ICP-OES (major elements) and ICP-MS (trace elements) of the solutions obtained after mineral digestion.

Teeth samples

Two sets of tooth enamel samples were analyzed during this study to evaluate the proposed matrix-matched calibration procedure *versus* external standard method based on NIST 610. These samples represented: (i) five archaeological teeth (S_A1, S_A2, S_A3, S_A4, S_A5) dated back to the 16th century with no specific historical context, and (ii) five modern primary teeth (S_M1, S_M2, S_M3, S_M4, S_M5). Historic teeth were subjected to point laser ablation without preparation while modern samples were prepared in the form of cross-sections embedded in resin and microsampled with line laser ablation.

Certified Reference Materials

BCR-32 (http://irmm.jrc.ec.europa.eu/) and NIST NBS 120b phosphate rock [27] were used for quality control of the results during bulk analysis of apatite samples by ICP-OES and ICP-MS for major and trace elements. SRM NIST 1400 and SRM NIST 1486 (www.nist.gov) were used for quality control of the LA-ICP-MS results during analysis of both apatites and teeth samples. NIST 610 glass reference material was used for one of the LA-ICP-MS calibration approaches. Reference values for NIST 1400, NIST 1486 and NIST 610 were taken from GeoReM Geological and Environmental Reference Materials Database [28].

Instrumentation

ICP-OES (Optima 3300, Perkin Elmer) was used for major elements analysis and ICP-MS (Elan DRC-II, Perkin Elmer SCIEX, Canada) for trace elements determination in selected apatite crystals after their digestion. ICP-OES and DRC II ICP-MS systems were operated in their standard modes (Table 1). LA-ICP-MS (LSX-213 Nd:YAG laser ablation system, CETAC and NexION 300D, Perkin Elmer) was used for major, minor and trace elements analysis of archaeological teeth (point ablation mode), primary teeth (line ablation) and apatite crystals (point and line ablation modes) (Table 1).

Table 1. Instrumental setting and measurements conditions.

	ICP-MS (Elan 9000)	**ICP-MS (NexION 300D)**	**ICP-OES/MS**
Rf, power, W	1050	1250	1250
Plasma Ar gas flow rate, L min^{-1}	15	18	13
Auxiliary Ar gas flow rate, L min^{-1}	1.0	1.2	1.1
Carrier Argas flow rate, L min^{-1}	0.91	0.90	0.75
Dwell time per isotope, ms	10	10	100/50
	LSX-200+	**LSX-213**	-
Wavelength, nm	266	213	-
Ablation mode	point (n=7)	line (n=3)	-
Laser energy per pulse, mJ	5	5	-
Pulserepetitionrate, Hz	10	20	-
Beamdiameter, μm	100	100	-
Burstscounts	600	-	-
Scan rate, μm s^{-1}	-	25	-

ICP-OES and ICP-MS procedure

Before ICP-OES and ICP-MS measurements the apatites as well as SRM's phosphate rocks: BCR-32 and NBS 120b were powdered and fused with Li-metaborate ($LiBO_2$) or sintered with sodium peroxide, then dissolved in 0.5 mol/L nitric acid and diluted to the appropriate concentration. Rh and Re were used as internal standards for ICP-MS, Sc was selected as an internal standard for ICP-OES measurements. The solutions obtained from Li-metaborate fusion were used during the analysis of major and minors elements (Na, Si, P, Ca, Al and Fe) by means of ICP-OES, whereas the solutions obtained after sintering with sodium peroxide were used during analysis of trace elements (Li, Mg, Cl, V, Cr, Mn, Ni, Cu, Zn, Rb, Sr, Mo, Cd, Sb, Ba, REE, Pb, Th and U) by ICP-MS.

LA-ICP-MS procedure

The surfaces of the remaining solid parts of all crystals as well as NIST 610 were cleaned by sonication in double distilled water for 15 minutes, then the samples were inserted into acetone (p.f.a., POCh Poland) and sonicated during 15 minutes to eliminate any organic and inorganic contaminations. Afterwards the samples were air-dried and placed in the ablation cell. Teeth samples were analyzed without any pretreatment. Ablation was executed from the locations selected carefully to omit inclusions visible at the surface of apatites. Transient signals were recorded for the following isotopes: ^{7}Li, ^{23}Na, ^{26}Mg, ^{27}Al, ^{29}Si, ^{31}P, ^{35}Cl, ^{42}Ca, ^{43}Ca, ^{51}V, ^{53}Cr, ^{55}Mn, ^{57}Fe, ^{61}Ni, ^{65}Cu, ^{66}Zn, ^{85}Rb, ^{88}Sr, ^{95}Mo, ^{111}Cd, ^{121}Sb, ^{137}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{151}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{173}Yb, ^{175}Lu, ^{208}Pb, ^{232}Th and ^{238}U. For all LA-ICP-MS measurements, the samples were placed inside the ablation cell together with NIST SRM 610 (www.nist.gov). The standard was measured twice in the beginning and twice at the end of each measurement run to correct for instrumental drift. For each sample either 7 single point ablations (archaeological teeth) or 3 single line ablations (modern primary teeth) were executed and the registered transient signals were then used for quantification. For apatites both ablation modes (point and line) were applied to investigate the homogeneity of the minerals. Line ablation was performed after pre-ablation laser cleaning to avoid surface contamination. The LA-ICP-MS signals were background corrected, integrated and recalculated with ^{42}Ca as the internal standard [24,27-29]. All results were normalized to 100 wt.% [30,31]. The assumption was made about the constant content of CaO equal to ca. 55.5 % in apatites [27]. Such estimations are widely used during analysis of minerals [29,31], moreover this particular value was then justified by the results obtained from the bulk analysis (Table 2). The criterion of 5% precision was used for the measurements performed under optimized LA-ICP-MS conditions.

Table 2. Quantitative data representing bulk elemental composition of the investigated apatites (the content of elements is expressed in mg/kg, oxides in wt. %).

	A1 Mean ± SD	**A2** Mean ± SD	**A3** Mean ± SD	**A4** Mean ± SD	**A5** Mean ± SD
Li 2)	1.2 ± 0.2	2.6 ± 0.4	< LOD	0.23 ± 0.2	0.56 ± 0.3
Na_2O 1)	0.29 ± 0.20	0.22 ± 0.10	0.14 ± 0.10	0.11 ± 0.10	0.27 ± 0.10
Mg 2)	181 ± 3	75.9 ± 5.0	50.9 ± 4.0	42.1 ± 2.0	143 ± 22
Al 2)	0.61 ± 0.4	9.6 ± 1.2	10 ± 2	5.1 ± 0.9	41 ± 9
SiO_2 1)	0.23 ± 0.12	0.38 ± 0.17	0.53 ± 0.19	0.52 ± 0.16	0.36 ± 0.11
P_2O_5 1)	42.6 ± 0.1	41.0 ± 0.1	42.7 ± 0.1	43.1 ± 0.1	42.0 ± 0.1
Cl 2)	2697 ± 30	1424 ± 7	3019 ± 20	2815 ± 30	738 ± 10
CaO1)	54.3 ± 0.6	54.5 ± 0.6	55.4 ± 1.2	56.4 ± 0.8	55.2 ± 0.7
V 2)	24.0 ± 0.5	15.3 ± 0.2	34.4 ± 0.3	30.9 ± 0.6	18.7 ± 0.3
Mn 2)	118 ± 1	45 ± 2	163 ± 4	128 ± 4	62 ± 1
Fe 1)	333 ± 4	56.6 ± 1.0	260 ± 3	218 ± 3	75.6 ± 2.4
Zn 2)	1.7 ± 0.1	1.2 ± 0.1	< LOD	3.1 ± 0.2	1.2 ± 0.2
Rb 2)	<LOD	<LOD	0.13 ± 0.1	0.10 ± 0.09	0.27 ± 0.1
Sr 2)	467 ± 1	1138 ± 1	817 ± 1	845 ± 1	1464 ± 18
Ba 2)	7.0 ± 0.2	10.1 ± 0.4	1.8 ± 0.2	1.0 ± 0.1	97.3 ± 1.0
La 2)	2900 ± 74	64.1 ± 0.7	1621 ± 30	1339 ± 20	194 ± 5
Ce 2)	4200 ± 130	135 ± 9	2400 ± 48	2300 ± 65	332 ± 7
Pr 2)	356 ± 9	14.5 ± 0.2	275 ± 5	243 ± 7	30.2 ± 0.7
Nd 2)	1093 ± 20	54.3 ± 0.7	957 ± 16	859 ± 20	102 ± 2
Sm 2)	135 ± 2	10.5 ± 0.2	194 ± 4	179 ± 3.5	16.9 ± 0.2
Eu 2)	16.4 ± 0.4	2.3 ± 0.1	29.3 ± 0.5	28.6 ± 0.5	3.8 ± 0.1
Gd 2)	148± 4	10.4 ± 0.2	209 ± 3	196 ± 4	17.1 ± 0.4
Tb 2)	13.0 ± 0.3	1.6 ± 0.1	30.0 ± 0.4	29.8 ± 0.6	2.5 ± 0.2
Dy 2)	74.5 ± 1.4	8.7 ± 0.2	169 ± 2	164 ± 5	13.6 ± 0.3
Ho 2)	14.0 ± 0.3	1.7 ± 0.1	32.9 ± 0.6	31.8 ± 1.0	2.6 ± 0.2
Er 2)	37.0 ± 0.8	4.7 ± 0.2	91.3 ± 1.6	88.1 ± 2.0	7.5 ± 0.2
Tm2)	4.6 ± 0.2	0.6 ± 0.1	11.1 ± 0.1	10.7 ± 0.1	0.9 ± 0.1
Yb 2)	26.6 ± 0.4	3.5 ± 0.2	60.6 ± 1.0	60.6 ± 1.3	5.6 ± 0.2
Lu 2)	3.7 ± 0.2	0.5 ± 0.1	7.1 ± 0.2	7.2 ± 0.3	0.7 ± 0.1
Pb2)	0.7 ± 0.1	11.0 ± 0.3	3.3 ± 0.2	3.1 ± 0.2	9.6 ± 0.2
Th2)	184 ± 1	170 ± 4	210 ± 4	194 ± 5	147 ± 2
U 2)	9.3 ± 0.2	83.6 ± 2.4	21.7 ± 0.8	20.0 ± 0.7	62.8 ± 1.4

1) ICP-OES; 2) ICP-MS

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Results and Discussion

The aliquots obtained after digestion of the first halves of apatite crystals were analyzed in respect of their elemental bulk composition by means of ICP-OES and ICP-MS. The obtained quantitative data are given in Table 2 giving the overview of the variable range of content of different elements in the crystals.

The remained halves of the apatite crystals were analyzed by LA-ICP-MS. Line ablation on the solid apatite samples was performed in order to estimate the degree of heterogeneity of the analyzed crystals. The majority of monitored isotopes were distributed homogeneously in the apatites, however some exceptions could be noticed (Na, Si, Al and Th) (Fig.1). Al was the most heterogeneous element among the investigated ones and it was excluded from the further investigations.

Seven repetitive single spot ablations were executed from each mineral sample and the averaged results of all selected elements in 5 apatite standards were calculated. Assuming the general macroscopic homogenous bulk composition of the entire apatite crystal, the results of ICP-OES/MS measurements were then used as the known content of the respective elements in particular apatite crystal for the further investigations. The linear through zero calibration curves were constructed for each element with the reference values recalling data of the ICP-OES/MS analysis from Table 2. Calculated correlation coefficient values varied from no correlation (^{85}Rb, ^{137}Ba, ^{232}Th) to 0.9833 (^{151}Eu) if all apatite standards were recalled. The noticeable increase of the correlation coefficient values for the most elements regardless ablation mode was observed after rejection of the two most apparent outliers from each calibration curve (Table 3).

Due to variable elemental compositions of the mineral samples, the outliers originated from different crystals and the final calibration curves based on different apatite samples. The final 3-point calibration curves were characterized by the correlation coefficient values in the range of 0.4819 for ^{232}Th to 0.9998 for ^{163}Dy and ^{173}Yb (Table 3). These values were even better if line ablation would be applied resulting in the R^2 value from 0.6563 for ^{232}Th to 0.9997 for ^{139}La. The data presented in Table 3 refers to elemental analysis of 5 natural crystals selected ad-hoc. They represented random chemical composition, but according to the literature data a wider range of elemental concentrations can be expected in natural apatite crystals [32], therefore a careful selection and evaluation of other crystals would broaden the working range of the proposed matrix-matched calibration approach.

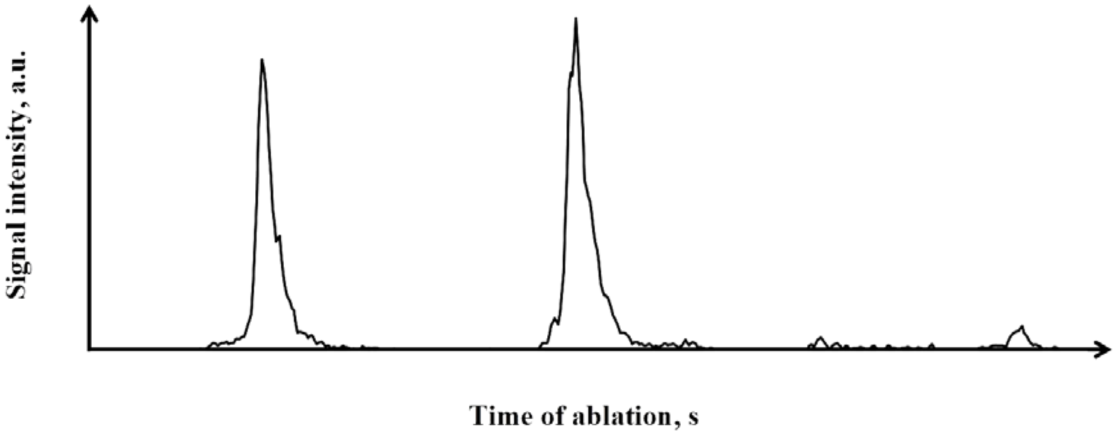

Fig. 1. Transient signal registered for ^{37}Al during line ablation of the most heterogeneous apatite crystal.

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Table 3. R^2 values for apatites calibration curves constructed based on 5 or 3 points using both ablation modes.

	point ablation		**line ablation**
	5-point calibration	**3-point calibration**	**3-point calibration**
Li	0.9111	0.9685	0.9250
Na	0.5524	0.8841	0.9565
Mg	0.7303	0.9349	0.9929
Si	0.4017	0.9533	0.9356
Cl	0.3911	0.8739	0.9783
V	0.5213	0.8925	0.9902
Mn	0.8142	0.9848	0.9343
Fe	0.8150	0.9941	0.9869
Zn	0.4901	0.7337	0.9789
Rb	-	0.9102	0.9606
Sr	0.9652	0.9884	0.9993
Ba	-	0.9886	0.9600
La	0.9299	0.9985	0.9997
Ce	0.9983	0.9996	0.9911
Pr	0.9331	0.9994	0.9609
Nd	0.9301	0.9985	0.9975
Sm	0.9068	0.9984	0.9279
Eu	0.9972	0.9994	0.9721
Gd	0.9032	0.9981	0.9941
Tb	0.9098	0.9958	0.9860
Dy	0.8948	0.9998	0.9694
Ho	0.8820	0.9995	0.9752
Er	0.8684	0.9987	0.9790
Tm	0.8573	0.9994	0.9815
Yb	0.8939	0.9998	0.9789
Lu	0.8843	0.9996	0.9583
Pb	0.7251	0.9651	0.9758
Th	-	0.4819	0.6563
U	0.9716	0.9983	0.9980

Evaluation of the necessity for using matrix-matched calibration

The usefulness of the proposed calibration approach was evaluated by comparison to the external calibration method with NIST 610 in elemental analysis of the selected certified reference materials: NIST 1400 (bone ash) and NIST 1486 (bone meal). The results obtained for both CRMs against either NIST 610 or apatites are within their standards deviation for the most of elements (Table 4). The use of the apatite calibration approach was beneficial for quantification of some elements (Na, Mg, Si, Cl, V, Sr and Ba), while for the others (Rb and Th) the calibration range and linearity of the calibration curve was not sufficient.

Table 4. Comparison of the quantification data obtained according to apatites calibration approach vs. NIST 610 (oxides are expressed in wt.%, elements - in mg/kg).

		NIST 1400			**NIST 1486**		
Element	**LOD**	**Reference values**	**NIST 610 calibration**	**Apatite calibration**	**Reference values**	**NIST 610 calibration**	**Apatite calibration**
Li	0.094	0.95	1.39 ± 0.28	0.60 ± 0.10	-	1.69 ± 0.21	0.76 ± 0.10
Na_2O	0.00001	0.810	1.090 ± 0.170	0.840 ± 0.130	0.675	1.026 ± 0.021	0.790 ± 0.020
Mg	0.052	6840	8735 ± 276	6775 ± 214	4660	5609 ± 217	4391 ± 170
SiO_2	0.0072	0.278	0.310 ± 0.150	0.250 ± 0.120	0.043	0.080 ± 0.010	0.067 ± 0.008
P_2O_5	0.0005	41.01	43.37 ± 1.39	43.79 ± 1.40	28.17	26.50 ± 0.52	27.01 ± 0.53
Cl	129	263.5	443 ± 185	293 ± 122	-	552 ± 93	369 ± 62
V	0.13	0.769	0.960 ± 0.560	0.870 ± 0.510	-	<LOD	<LOD
Mn	0.062	17	17 ± 2	20 ± 3	1	1.6 ± 0.3	2.0 ± 0.5
Fe	3.0	660	569 ± 282	455 ± 226	99	145 ± 27	117 ± 22
Rb	0.019	0.71	0.47 ± 0.06	0.16 ± 0.02	<0.9	0.46 ± 0.05	0.15 ± 0.02
Sr	0.018	249	391 ± 21	309 ± 17	264	392 ± 30	313 ± 24
Ba	0.14	240	349 ± 11	306 ± 10	189	404 ± 35	357 ± 31
La	0.01	0.386	0.370 ± 0.090	0.250 ± 0.060	-	0.036 ± 0.012	0.024 ± 0.008
Ce	0.009	0.821	0.630 ± 0.140	0.480 ± 0.110	0.02	0.38 ± 0.21	0.29 ± 0.16
Pr	0.009	0.086	0.070 ± 0.020	0.060 ± 0.020	-	<LOD	<LOD
Nd	0.06	0.316	0.260 ± 0.070	0.220 ± 0.060	-	<LOD	<LOD
Sm	0.07	0.0595	<LOD	<LOD	-	<LOD	<LOD
Eu	0.02	0.030	0.033 ± 0.004	0.029 ± 0.004	0.02	<LOD	<LOD
Gd	0.08	0.064	0.090 ± 0.030	0.090 ± 0.030	-	<LOD	<LOD
Tb*	0.01	0.0096	<0.02	<0.02	-	<LOD	<LOD
Dy	0.05	0.0479	0.08 ± 0.07	0.08 ± 0.07	-	<LOD	<LOD
Ho	0.01	0.0105	0.02 ± 0.01	0.02 ± 0.01	-	<LOD	<LOD
Er	0.03	0.0254	0.03 ± 0.02	0.03 ± 0.02	-	0.03 ± 0.01	0.03 ± 0.01
Tm	0.01	0.0034	<LOD	<LOD	-	<LOD	<LOD
Yb	0.09	0.0183	0.11 ± 0.05	0.011 ± 0.05	-	<LOD	<LOD
Lu	0.01	0.009	0.02 ± 0.01	0.02 ± 0.01	-	0.01 ± 0.01	0.01 ± 0.01
Pb	0.09	9.07	10 ± 6	11 ± 7	1.335	2.2 ± 0.8	2.4 ± 0.8
Th*	0.02	0.123	<0.49	<0.56	0.0052	<LOD	<LOD
U	0.01	0.066	0.14 ± 0.06	0.16 ± 0.06	0.028	0.03 ± 0.02	0.04 ± 0.02

* – the most heterogeneously distributed elements

The investigations of pelletized NIST 1400 and NIST 1486 were accompanied by elemental analysis of enamel teeth samples (Table 5 and Table 6).

The comparison of quantitative results recalculated either in respect to NIST 610 or matrix-matched apatite calibration indicated that majority of elemental information remained coherent within their standard deviations regardless the procedure of applied quantification. The highest consistency of the results was observed for rare earth elements (REEs). The quantification of Na, Mg and Cl in all samples was underestimated if they were calculated *vs* NIST 610 as the external standard, therefore for these elements the use of apatite calibration approach allowed to increase the accuracy of the undertaken measurements.

Table 5. Comparison of the quantitative data of archaeological teeth analysis resulted from either recalculation vs NIST 610 or apatite-calibration approach (oxides expressed wt. %, elements - in mg/kg).

	S_A1		**S_A2**		**S_A3**		**S_A4**		**S_A5**	
	NIST 610 Calibration	**Apatites calibration**	**NIST 610 calibration**	**Apatites calibration**	**NIST 610 Calibration**	**Apatites Calibration**	**NIT 610 calibration**	**Apatites calibration**	**NIST 610 calibration**	**Apatites Calibration**
Li	1.4 ± 1.3	0.63 ±0.60	1.5 ± 0.3	0.65 ± 0.16	0.39 ± 0.17	0.18 ± 0.1	0.77 ± 0.29	0.34 ± 0.13	1.04 ± 0.27	0.47 ± 0.12
Na_2O	0.93 ± 0.08	0.72 ± 0.06	0.71 ± 0.02	0.55 ± 0.02	0.79 ± 0.04	0.61 ± 0.03	0.89 ± 0.04	0.68 ± 0.03	0.67 ± 0.03	0.51 ± 0.02
Mg	2551 ± 203	1983 ± 158	1948 ± 100	1519 ± 78	2020 ± 138	1576 ± 108	2111 ± 116	1643 ± 90	1803 ± 187	1402 ± 146
SiO_2	0.11 ± 0.09	0.08 ± 0.07	0.07 ± 0.02	0.06 ± 0.01	0.14 ± 0.12	0.11 ± 0.10	0.08 ± 0.05	0.07 ± 0.04	0.07 ± 0.02	0.05 ± 0.02
P_2O_5	44.54 ± 3.25	45.07 ± 3.29	44.44 ± 1.89	45.11 ± 1.91	44.32 ± 2.19	45.01 ± 2.22	44.49 ± 2.07	45.06 ± 2.10	44.78 ± 2.78	45.31 ± 2.81
Cl	4368 ± 1233	2896 ± 817	8176 ± 670	5437 ± 445	7196 ± 883	4787 ± 587	6482 ± 578	4302 ± 383	5680 ± 429	3765 ± 284
V	1.2 ± 0.9	1.0 ± 0.8	0.3 ± 0.2	0.18 ± 0.16	1.0 ± 0.3	0.91 ± 0.25	0.57 ± 0.18	0.52 ± 0.16	0.22 ± 0.17	0.20 ± 0.16
Mn	42 ± 17	51 ± 20	6 ± 2	7 ± 2	35 ± 16	42 ± 19	12 ± 7	14 ± 8	11 ± 2	13 ± 3
Fe	68 ± 15	55 ± 12	37 ± 5	30 ± 4	73 ± 35	59 ± 28	108 ± 30	86 ± 24	71 ± 19	57 ± 15
Rb	0.14 ± 0.10	-	0.11 ± 0.06	-	0.13 ± 0.06	-	0.16 ± 0.07	-	0.17 ± 0.07	-
Sr	144 ± 13	114 ± 10	139 ± 12	111 ± 10	102 ± 13	81 ± 10	219 ± 17	174 ± 13	180 ± 15	143 ± 12
Ba	11 ± 2	9.8 ± 1.8	5 ± 1	4.6 ± 0.9	3.0 ± 0.8	2.7 ± 1	13 ± 2	11 ± 2	5 ± 2	4.5 ± 1.7
La	0.27 ± 0.26	0.18 ± 0.15	0.04 ± 0.04	0.03 ± 0.02	0.19 ± 0.09	0.13 ± 0.06	0.52 ± 0.44	0.35 ± 0.30	6.0 ± 5.9	4.0 ± 3.9
Ce	0.20 ± 0.19	0.15 ± 0.14	0.08 ± 0.05	0.06 ± 0.05	0.33 ± 0.21	0.26 ± 0.16	0.33 ± 0.27	0.26 ± 0.21	0.47 ± 0.39	0.36 ± 0.34
Pr	0.08 ± 0.08	0.07 ± 0.06	0.01 ± 0.01	0.01 ± 0.01	0.06 ± 0.05	0.05 ± 0.04	0.09 ± 0.08	0.07 ± 0.07	1.2 ± 1.1	0.9 ± 0.8
Nd	0.46 ± 0.30	0.39 ± 0.26	0.15 ± 0.12	0.13 ± 0.12	0.29 ± 0.08	0.25 ± 0.07	0.42 ± 0.33	0.36 ± 0.28	5.2 ± 5.1	4.4 ± 4.2
Sm	0.10 ± 0.05	0.08 ± 0.04	<LOD	<LOD	0.17 ± 0.05	0.15 ± 0.04	0.15 ± 0.07	0.13 ± 0.06	1.0 ± 0.8	0.8 ± 0.7
Eu	0.05 ± 0.02	0.04 ± 0.01	0.03 ± 0.02	0.03 ± 0.02	0.05 ± 0.04	0.05 ± 0.04	0.03 ± 0.03	0.02 ± 0.03	0.23 ± 0.22	0.21 ± 0.20
Gd	0.29 ± 0.25	0.28 ± 0.24	0.11 ± 0.06	0.11 ± 0.06	0.25 ± 0.24	0.24 ± 0.23	0.20 ± 0.14	0.19 ± 0.14	1.1 ± 1.1	1.0 ± 0.9
Tb	0.04 ± 0.03	0.04 ± 0.03	0.02 ± 0.01	0.02 ± 0.01	0.05 ± 0.05	0.05 ± 0.05	0.02 ± 0.02	0.02 ± 0.02	0.17 ± 0.13	0.17 ± 0.12
Dy	0.16 ± 0.16	0.16 ± 0.15	0.06 ± 0.04	0.06 ± 0.04	0.13 ± 0.11	0.13 ± 0.11	0.08 ± 0.06	0.08 ± 0.06	1.0 ± 0.9	1.0 ± 0.9
Ho	0.02 ± 0.02	0.02 ± 0.02	0.01 ± 0.01	0.01 ± 0.01	0.04 ± 0.03	0.03 ± 0.03	0.02 ± 0.02	0.02 ± 0.02	0.20 ± 0.19	0.19 ± 0.18
Er	0.17 ± 0.13	0.17 ± 0.13	0.04 ± 0.01	0.04 ± 0.01	0.10 ± 0.09	0.09 ± 0.08	0.06 ± 0.05	0.06 ± 0.05	0.6 ± 0.5	0.6 ± 0.5
Tm	0.03 ± 0.02	0.03 ± 0.02	0.02 ± 0.01	0.01 ± 0.01	0.03 ± 0.02	0.03 ± 0.02	0.02 ± 0.02	0.02 ± 0.02	0.11 ± 0.10	0.10 ± 0.09
Yb	0.38 ± 0.37	<LOD	0.13 ± 0.11	<LOD	0.21 ± 0.20	<LOD	0.14 ± 0.13	<LOD	0.54 ± 0.50	<LOD
Lu	0.05 ± 0.05	0.06 ± 0.05	0.05 ± 0.04	0.06 ± 0.04	0.04 ± 0.04	0.04 ± 0.05	0.02 ± 0.02	0.02 ± 0.02	0.08 ± 0.07	0.09 ± 0.07
Pb	11 ± 6	12 ± 7	1.6 ± 0.7	1.7 ± 0.8	91 ± 30	100 ± 33	50 ± 19	54 ± 21	9 ± 2	10 ± 2
Th	0.09 ± 0.07	0.10 ±0.08	0.03 ± 0.02	0.03 ± 0.02	0.05 ± 0.05	0.05 ± 0.05	0.05 ± 0.03	0.06 ± 0.04	0.09 ± 0.04	0.10 ± 0.05
U	0.04 ± 0.02	0.05 ± 0.03	0.02 ± 0.02	0.02 ± 0.02	0.10 ± 0.09	0.12 ± 0.10	0.22 ± 0.14	0.25 ± 0.16	0.14 ± 0.12	0.16 ± 0.15

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Table 6. Comparison of usefulness of apatites vs. NIST 610 (oxides in wt. %, rest in mg/kg) calibration based on the exemplary modern primary tooth enamel samples.

	S_M1		**S_M2**		**S_M3**		**S_M4**		**S_M5**	
	NIST 610 Calibration	**Apatites calibration**	**NIST 610 calibration**	**Apatites calibration**	**NIST 610 Calibration**	**Apatites Calibration**	**NIST 610 calibration**	**Apatites calibration**	**NIST 610 calibration**	**Apatites Calibration**
Na_2O	1.01 ± 0.04	0.85 ± 0.04	0.99 ± 0.6	0.84 ± 0.05	0.69 ± 0.05	0.49 ± 0.03	0.84 ± 0.06	0.69 ± 0.05	0.78 ± 0.03	0.60 ± 0.02
Mg	4138 ± 330	3037 ± 220	3838 ± 435	2990 ± 293	10187 ± 912	9181 ± 822	3266 ± 317	2244 ± 205	4066 ± 357	2879 ± 253
SiO_2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
P_2O_5	42.39 ± 2.56	42.92 ± 2.59	42.46 ± 3.00	43.33 ± 3.08	42.21 ± 3.59	42.85 ± 3.57	42.12 ± 2.77	43.04 ± 2.83	42.03 ± 3.75	43.15 ± 3.88
Cl	1562 ± 207	1152 ± 153	2074 ± 465	1417 ± 318	1219 ± 125	817 ± 111	3421 ± 487	2246 ± 320	3039 ± 434	2182 ± 227
Mn	8 ± 2	9 ± 2	2 ± 1	3 ± 1	1 ± 0	2 ± 1	5 ± 1	6 ± 2	<LOD	<LOD
Fe	<LOD	<LOD	<LOD	<LOD	49 ± 24	31 ± 15	42 ± 10	39 ± 10	75 ± 33	73 ± 31
Sr	288 ± 15	268 ± 14	140 ± 13	132 ± 12	184 ± 14	142 ± 11	120 ± 12	108 ± 10	159 ± 15	146 ± 14
Ba	5 ± 2	4 ± 2	3 ± 1	2 ± 1	12 ± 2	9 ± 2	<LOD	<LOD	<LOD	<LOD

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Conclusions

The use of natural apatite crystals as matrix matched standards for LA-ICP-MS analysis of bone tissues was proposed and evaluated in this work. Natural apatite samples are easily accessible minerals with the general chemical characteristics similar to bone tissue, therefore they could be used for calibration of LA-ICP-MS for analysis of tooth enamel samples with no special pretreatment. The composition of tooth enamel available for LA-ICP-MS measurements could be useful for fast, micro-destructive screening of elemental similarities of archaeological samples. The orthodontic treatments that use variable modern metal alloys could be also evaluated by using the proposed matrix-matched calibration approach for investigations of tooth enamel models.

Several natural crystals were inspected in respect of their elemental bulk composition as well as the distribution of the selected elements within the investigated crystals. ICP-OES and ICP-MS were used for the determination of the content of selected elements and the obtained values were considered the target values for the optimization of the consequent LA-ICP-MS measurements. Although, the results of direct analysis of solid samples by LA-ICP-MS were influenced by the heterogeneity of their distribution, repetitive spot (n=7) or line (n=3) analyses assured reliable averaged results for the most of the investigated elements. Heterogeneous distribution and relatively very low concentration of Al, Rb, Th and Zn excluded the possibility to use LA-ICP-MS for reliable quantification of these elements in accordance to the proposed analytical procedure.

Elemental composition of NIST 1400 and NIST 1486 bone reference materials was determined by the LA-ICP-MS using either NIST 610 or apatite calibration approach and compared to the reference values. During validation of the procedure the data obtained for archaeological and modern samples confirmed usefulness of natural apatite crystals as in-house reference materials. The proposed calibration procedure based on the use of natural apatite crystals can be applied for the analysis of bone tissues by means of LA-ICP-MS with some restriction. The main advantage of the described analytical approach relied on a fast selection of best standard materials if the appropriate number of apatite samples would be tested.

The use of natural apatites matrix matched calibration for quantitative analysis of osseous tissues was evaluated. Although the matrix effects were not found prevailing for the final results of the most of the investigated elements, the use of apatites was beneficial for quantification of Na, Mg and Cl in tooth enamel. It can be expected that the usefulness of the apatite crystals calibration approach would increase for the greater number of tested apatite samples. Screening of their elemental composition would allow to select the most divergent crystals in respect to their elemental composition, leading to increase the calibration reliability and extension of the dynamic range for most of the elements. Based on this work it can be concluded that even 5 natural apatites could be successfully used as the solid matrix matched home standards for calibration approach devoted to elemental analysis of osseous samples by means of laser ablation ICP-MS.

References

1. Günther, D.; Jackson, S. E.; Longerich, H.P. *Spectrochim. Acta B* **1999**, *54*, 381-409 DOI: https://doi.org/10.1016/S0584-8547(99)00011-7
2. Russo, R. E.; Mao, X. L.; Liu, H. C.; Gonzalez, J.; Mao, S. S. *Talanta* **2002**, *57*, 425-451 DOI: https://doi.org/10.1016/S0039-9140(02)00053-X
3. Jochum, K. P.; Stoll, B.; Weis, U.; Jacob, D. E.; Mertz-Kraus, R.; Andreae, M. O. *Geostand. Geoanal. Res.* **2014**, *38*, 265-292 DOI: 10.1111/j.1751-908X.2014.12028.x
4. Jarvis, K. E.; Williams, J. G.; *Chem. Geol.* **1993**, *106*, 251-262, DOI: https://doi.org/10.1016/0009-2541(93)90030-M
5. Tang, M.; McDonough, W. F.; Arevalo, R. *J. Anal. At. Spectrom.* **2014**, *29*, 1835-1843, DOI: http://dx.doi.org/10.1039/C4JA00155A
6. Günther, D.; Quadt, A. V.; Wirz, R.; Cousin, H.; Dietrich, V. J. *Mikrochim. Acta* **2001**, *136*, 101-107, DOI: https://doi.org/10.1007/s006040170038

7. Pozebon, D.; Scheffler, G. L.; Dressler, V. L.; Nunes, M. A. G. *J. Anal. At. Spectrom.* **2014**, *29*, **2204-2228, DOI:** http://dx.doi.org/10.1039/C4JA00250D
8. Urgast, D. S.; Feldmann, J. *J. Anal. At. Spectrom.* **2013**, *28*, **1367-1371, DOI:** http://dx.doi.org/10.1039/C3JA50058F
9. Becker, J. S.; Zoriy, M.; Becker, J. S.; Dobrowolska, J.; Matusch, A. *J. Anal. At. Spectrom.* **2007**, *22*, **736-744, DOI:** http://dx.doi.org/10.1039/B701558E
10. Giussani, B.; Monticelli, D.; Rampazzi, L. *Anal. Chim. Acta* **2009**, *635,* 6-21 DOI: 10.1016/j.aca.2008.12.040
11. Gruhl, S.; Witte, F.; Vogt, J.; Vogt, C. *J. Anal. At. Spectrom.* **2009**, *24,* 181-188, DOI: http://dx.doi.org/10.1039/B813734J
12. Pakieła, M.; Wojciechowski, M.; Wagner, B.; Bulska, E. *J. Anal. At. Spectrom*. **2011**, *26,* 1539-1543, DOI: http://dx.doi.org/10.1039/C0JA00201A
13. Gilbert, S.; Danyushevsky, L.; Robinson, P.; Wohlgemuth-Ueberwasser, C.; Pearson, N.; Savard, D.; Norman, M.; Hanley, J. *Geostand. Geoanal. Res.* **2013**, *37,* 51–64 DOI: 10.1111/j.1751-908X.2012.00170.x
14. Ødegård, M.; Mansfeld, J.; Dundas, S. H. *Fres. J. Anal. Chem.* **2001**, *370*, 819–827 DOI: http://dx.doi.org/10.1039/B100899O
15. Kellett, L. C.; Golitko, M.; Bauer, B. S. *J. Arch. Sc.* **2013**, *40*, 1890-1902 DOI: https://doi.org/10.1016/j.jas.2012.11.014
16. Comodi, P.; Buccianti, A.; Zucchini, A.; Merletti, M.; Bergamini, M.; Nazzareni, S. *Archeom.* **2014**, *56,* 58-77 DOI: 10.1111/arcm.12068
17. Yong Sheng, L.; Zhao Chu, H.; Ming, L.; Shan, G. *Chin. Sc. Bull.* **2013**, *58*, 3863-3878 DOI: 10.1007/s11434-013-5901-4
18. Reiche, I.; Favre-Quattropani, L.; Calligaro, T.; Salomon, J.; Bocherens, H.; Charlet, L.; Menu, M. *Nucl. Instr. Meth. Phys. Res. B* **1999**, *150*, 656-662 DOI: https://doi.org/10.1016/S0168-583X(98)00949-5
19. McClellan, G.; Lehr, J. R. *American Mineralogist* **1969**, *54*, 1374-1379
20. Piccoli, P. M.; Candela, P. A., in: *Phosphates: Geochemical, Geobiological, and Materials Importance,* Kohn, M. J.; Rakovan, J.; Hughes J. M., **2002**, *31*, 255-292
21. Deer, W. A.; Chang, L. L. Y.; Howie, R. A.; Zussman, J. *Rock-forming minerals*, Ed. Geological Society, 1996
22. Kohn, M. J.; Schoeninger, M. J.; Barker, W. W. *Geochim. Cosmochim. Acta* **1999**, *63,* 2737-2747 DOI: https://doi.org/10.1016/S0016-7037(99)00208-2
23. Ghazi, A. M.; Shuttleworth, S.; Angulo, S. J.; Pashley, D. H *J. Anal. At. Spectrom.* **2000**, *15*, 1335-1341 DOI: http://dx.doi.org/10.1039/B001888K
24. Cucina, A.; Dudgeon, J.; Neff, H. *J. Arch. Sc.* **2007**, *34*, 1884-1888 DOI: https://doi.org/10.1016/j.jas.2007.01.004
25. Ugarte, A.; Unceta, N.; Pecheyran, C.; Goicolea, M. A.; Barrio, R. J. *J. Anal. At. Spectrom.* **2011**, *26,* 1421-1427 DOI: http://dx.doi.org/10.1039/C1JA10037H
26. Bellis, D. J.; Hetter, K. M.; Jones, J.; Amarasiriwardena, D.; Parsons, P. J. *J. Anal. At. Spectrom.* **2006**, *21,* 948-954 DOI: http://dx.doi.org/10.1039/B603435G
27. Govindaraju, K. *Geostand. Newsl.* **1994**, *18,* 331-331
28. http://georem.mpch-mainz.gwdg.de, accessed in July 2017
29. Gagnon, J. E.; Fryer, B. J.; Samson, I. M.; Williams-Jones, A. E. *J. Anal. At. Spectrom.* **2008**, *23,* 1529-1537 DOI: http://dx.doi.org/10.1039/B801807N
30. Halicz, L.; Günther, D. *J. Anal. At. Spectrom.* **2004**, *19*, 1539-1545 DOI: http://dx.doi.org/10.1039/B410132D
31. Liu, Y.; Hu, Z.; Gao, S.; Günther, D.; Xu, J.; Gao, C.; Chen, H. *Chem. Geol.* **2008**, *257*, 34-43 DOI: https://doi.org/10.1016/j.chemgeo.2008.08.004
32. Kempe, U.; Gotze, J. *Mineral. Mag.* **2002**, *66,* 151–172 DOI: 10.1180/0026461026610019