

Trace Elements in Landfill Calcite: a Comparison of Solution & Laser Ablation ICP-MS and Calibration to Different Standard Material (SRM NIST Glass and USGS MACS Carbonate)

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INTRODUCTION.

In last two decades many geochemical studies have used carbonate elemental composition as a proxy for the reconstruction of marine environment in geological history and for investigation of terrestrial or anthropogenic influences (e.g. Pena *et al.*, 2005; Hladil *et al.*, 2005; Ettler *et al.*, 2006). The analytical works are usually done by well established microprobe techniques, such as EPMA (electron microprobe) and/or sensitive laser ablation ICP-MS (inductively coupled plasma – mass spectrometry). However, the reliability of these analytical methods strongly depends on the availability of suitable and well-characterized reference materials. In contrast to solution methods, the microprobe techniques are frequently complicated by the requirement of a suitable calibration standard. The laboratories prepare usually own calibration materials (Craig *et al.*, 2000) or use commercially available glass standards (e.g. NISTs).

In this contribution, we present data on in situ trace element analysis in landfill calcites and on new USGS carbonate reference materials MACS-1 and MACS-2. The initial powder materials of these reference material represents synthetic carbonates doted by aliquote amount of trace elements and the reference data has not yet already been established. Two different methods were used to determine selected trace elements such as solution and laser ablation ICP-MS and the data obtained were mutually compared. Calcite

precipitating from landfill leachates are important carriers for trace elements, e.g. heavy metals and metalloids. The effect of calcite precipitation on contaminant controls in such anthropogenic environments was demonstrated in our previous studies (Ettler *et al.*, 2006). However, calcite is precipitating from leachate in small amounts, often preventing the classical solution ICP-MS analysis of trace elements. This study reports the verification of in situ trace element analysis by LA-ICP-MS.

SAMPLES.

Four calcite samples precipitating from leachate-polluted waters in the vicinity of an uncontrolled municipal landfill site at Dolní Chabry (Prague, Czech Republic) were collected. The samples were dried and pulverized and prepared for further analysis as powders and pressed pellets. X-ray diffraction analysis (XRD) confirmed the presence of pure calcite (Ettler *et al.*, 2006).

ANALYTICAL.

SOLUTION ICP-MS

The trace elements (Mg, Cr, Mn, Co, Ni, Cu, Zn, As, Sr, Cd, Ba, La, Ce, Nd, Pb, and U) in the MACS-1 and -2 reference materials and four naturally precipitated calcites K-1, K-2, K-3 and K-4 were determined using a modified total digestion in mineral acids (HNO₃ and HF) followed by conventional solution nebulization ICP-MS (VG PQ3). All the samples (and procedural blanks) were diluted before measurement by ICP-MS to minimize matrix effect.

The isotopes were selected with respect to their most abundant species, isobaric overlaps and minimum oxide interferences. Formation of oxides (MeO⁺/Me⁺) was monitored using a Ce solution and varied below a value of 0.008. The data were processed on-line using VG PlasmaLab software and applying corrections for instrumental drift and matrix effects. The count rates for the measured isotopes were corrected on the basis of interpolation of the ⁷⁴Ge, ¹⁰³Rh and ¹⁸⁷Re correction factors.

LASER ABLATION ICP-MS

Pressed pellets of natural calcites (K-1, K-2, K-3 and K-4) and MACS powder reference material samples were analysed for Mg, Cr, Mn, Co, Ni, Cu, Zn, As, Sr, Cd, Ba, La, Ce, Nd, Pb, and U with using laser ablation ICP-MS analysis without further modification. The analytical work was performed on the same equipment as solution analysis coupled to a NewWave 213 nm laser microprobe instaled at Charles University in Prague. The sample introduction system and calibration and correction strategy closely follow those as described by Strnad *et al.* (2005). SRM NIST 612 was used as an external calibration standard for in situ analyses of MACS-1 and MACS-2 reference material. The external calibration for measurement of landfill calcites (K-1 – K-4) were done using (i) MACS-1(2) with data obtained by laser ablation ICP-MS (see Table 1) and (ii) SRM NIST 612. The signals of ⁴³Ca and ⁴⁴Ca isotope contained in the analysed carbonate samples and calibration standards

palabras clave:

key words: trace elements, reference material, carbonate, laser ablation, ICP-MS

resumen SEM/SEA 2008

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were used to eliminate internal drift correction.

ppm	MACS-1 LA ICP-MS		MACS-2 LA ICP-MS	
	value N=20	SD	value N=20	SD
Mg			(40)	
Cr	112	9.1		
Mn	114	5.8	0.69	0.07
Co	114	5.7	3.07	0.07
Ni	108	8.1		
Cu	89	4.7	3.83	0.15
Zn	100	5.0	4.45	0.61
As			2.59	0.20
Sr	229	11.6	44.03	0.91
Cd	110	6.0	3.80	0.24
Ba	123	5.5	1.49	0.07
La	154	12.4	(0.10)	
Ce	118	6.3	(0.07)	
Nd	145	11.1	(0.06)	
Pb	109	7.8	62.57	5.68
U			1.30	0.07

Table 1. Laser ablation ICP-MS data for USGS MACS carbonate reference material

RESULTS/DISCUSSION.

Table 1 present the selected trace element data obtained by laser ablation ICP-MS in USGS MACS carbonate reference material. The analytical precision of individual laser ablation analysis varied between 5 and 20 % (RSD) for most elements in MACS-1 and up to 25 % (RSD) in MACS-2. The repeated analyses of both carbonate standard (N=20) yield a relative differences below 10%.

Figure 1 shows the trace element data obtained by solution and laser ablation ICP-MS in landfill calcite sample (K1). The solution ICP-MS

data represent the averages of three replicate decomposition (N=3) prepared for each sample. The average values calculated for all the calcite samples determined by laser ablation ICP-MS were calculated on the basis of ten replicates (N=10).

Good analytical precision of repeated analyses by laser ablation ICP-MS (given as one relative standard deviation; here 1 – 10 %) yield Mg, Mn, Co, Sr, Ba, U. The higher imprecision show data for transition metals (Cr, Co, Ni, Cu, Zn) and Pb; 5 - 15 % (RSD). Exception are data for lanthanoids (La, Ce, Nd) with analytical precision up to 100 % (RSD) in some cases. The precision obtained for conventional solution ICP-MS is, overall, better and does not exceed 10% relative for all analysed calcite samples.

The average concentrations measured by solution and laser ablation ICP-MS for each analysed calcite sample agree for Mn, Sr and Ba (up to 5% relative). Significant differences were found for other analysed elements depending on their low concentration, higher detection limit and/or possible inhomogeneities in naturally precipitated calcites (Fig. 1).

Difficulty that has frequently been mentioned by some authors is the formation of spectral interferences (e.g. Chrastný *et al.*, 2006). Problems may occur in the analysis of samples with very low metal contents (low ppm and sub-ppm level; e.g. $^{52}\text{Cr} \leftrightarrow ^{40}\text{Ar}^{12}\text{C}$, $^{59}\text{Co} \leftrightarrow ^{43}\text{Ca}^{16}\text{O}$, $^{60}\text{Ni} \leftrightarrow ^{44}\text{Ca}^{16}\text{O}$).

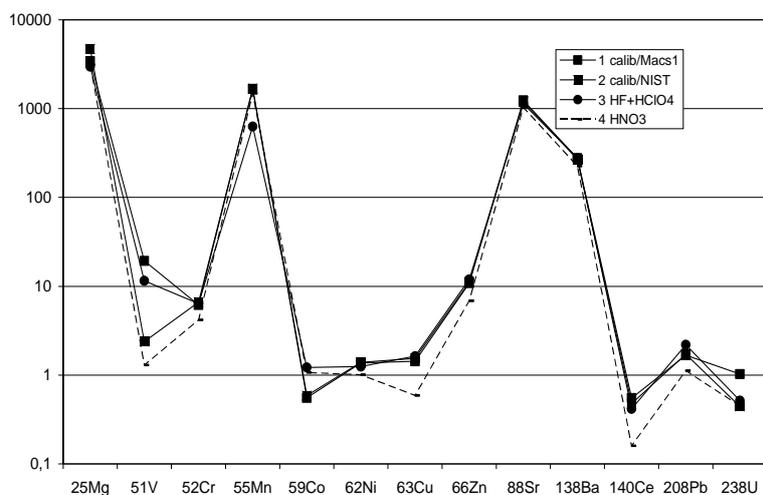


Fig. 1 Comparison of solution and LA ICP-MS data from landfill calcite sample K-1.

ACKNOWLEDGEMENTS

We would like to acknowledge Dr. Steven Wilson (USGS) for MACS reference materials. This study was financed by Ministry of Education, Youth and Sports (MSM 0021620855) and The Grant Agency of AS CR (IAA 300130702).

REFERENCES.

- Craig, C. N., Narcis, K.E., Clarke L.J. (2000): An assessment of calibration strategies for the quantitative and semi-quantitative analysis of calcium carbonate matrices by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). *J. Anal. At. Spectrom.*, **15**, 1001-1008.
- Ettler, V., Zelená, O., Mihaljevič, M., Šebek, O., Strnad, L., Coufal, P., Bezdička, P. (2006): Removal of trace elements from landfill leachate by calcite precipitation. *J. Geochem. Explor.*, **88**, 28-31.
- Hladil, J., Geršl, M., Strnad, L., Fráňa, J., Langrová, A., Spišiak, J. (2006): Stratigraphic variation of complex impurities in platform limestones and possible significance of atmospheric dust: a study with emphasis on GRS and MS outcrop logging (Eifelian-Frasnian, Moravia, Czech Republic). *Int. J. Earth Sci.*, **95**, 703-723.
- Pena, L.D., Calvo, E., Cacho, I., Eggins, S., Pelejero, C. (2005): Identification and removal of Mn-Mg-rich contaminant phases on foraminiferal test: Implications for Mg/Ca past temperature reconstructions. *Geochem. Geophys. Geosyst.*, **6** (9), 1-25.
- Strnad, L., Mihaljevič, M., Šebek, O. (2005): Laser ablation and solution ICP-MS determination of REE in USGS BIR-1G, BHVO-2G and BCR-2G glass reference materials. *Geostand. Geoanal. Res.*, **29**, 303-314.
- Chrastný, V., Komarek, M., Mihaljevič, M., Štichová J. (2006): Vanadium determination in chloride matrices using ICP-MS: finding the optimum collision/reaction cell parameters for suppressing polyatomic interferences. *Anal. Bioanal. Chem.* **385**, 962-970.