

QUANTIFICATION OF MATRIX EFFECTS DURING LA-ICP-MS ANALYSES OF TRACE ELEMENT ABUNDANCES IN IRON-RICH ALLOYS: IMPLICATIONS FOR METAL/SILICATE AND SULFIDE/SILICATE PARTITION COEFFICIENTS. J. Berndt¹, E.S. Steenstra¹⁻³, S. Klemme¹, W. van Westrenen³ (jberndt@uni-muenster.de) ¹Institute of Mineralogy, Münster University, Germany ²The Geophysical Laboratory, Washington D.C., United States, ³Vrije Universiteit Amsterdam, the Netherlands

Introduction: Metal and sulfide phases play an important role in planetary differentiation processes [e.g. 1,2]. Trace element concentrations in these phases are often measured using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Silicate reference materials are commonly used to calibrate LA-ICP-MS analyses of Fe-based samples [e.g. 3,4], mainly because homogeneous Fe-based standards that contain the elements of interests are scarce or practically non-existent. Commonly used systems employ 193 nm excimer ArF* lasers. It has been known for several decades that the use of these systems can result in large volatility-related fractionation during ablation, leading to significant matrix effects when using silicate-based calibrants for analyses of Fe-based samples [e.g. 5]. Here we quantify these effects and assess their effect on metal/silicate and sulfide/silicate partition coefficient determinations.

Methods: To assess the matrix effects arising from the use of silicate calibrant materials for LA-ICP-MS analyses of Fe-based samples, we compiled elemental concentrations of 19 elements in metals and sulfides reported in various experimental datasets from our laboratories [6-11]. Metals and sulfides were synthesized in equilibrium with silicate melts at high P - T using piston cylinder and/or multi-anvil presses in the high P laboratories of VU University Amsterdam, WWU Münster and the Geophysical Laboratory. Synthesized Fe-rich samples were characterized for major and minor elements using the same type of EPMA instruments at WWU Münster and Utrecht University. LA-ICP-MS analyses were all conducted at WWU Münster using an ArF* 193 nm excimer laser system. All medium resolution LA-ICP-MS analyses were calibrated using the NIST 612 glass, whereas the NIST 610 glass was used as the calibrant material for high resolution analyses specifically employed for the element P. All metal analyses were processed using EPMA-derived Ni or Si concentrations as an internal standard. Due to the absence of Ni or Si in sulfide samples, Cu concentrations were used as internal standard. These EPMA Cu abundances were corrected with the LA fractionation index obtained for Cu for metals,

Results: Comparison of the EPMA and LA-ICP-MS data shows that LA-ICP-MS consistently overestimates the abundance of volatile elements in metals and sulfides (Fig. 1). In contrast, the LA-ICP-MS derived concentrations of refractory elements such as Mo and

W are clearly underestimated relative to EPMA values (Fig. 2). The abundances of transitional (e.g. Ni, Co, Si) are well reproduced using both methods.

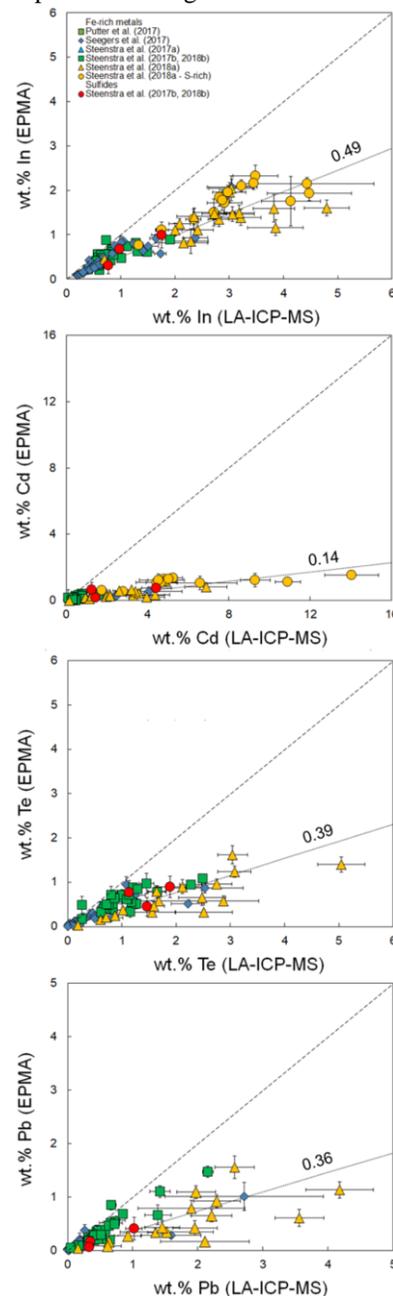


Fig. 1: Comparison between EPMA and LA-ICP-MS derived abundances of In, Cd, Te and Pb. Dashed lines are 1:1 identity lines plotted for reference. Solid lines are linear fits to the data assuming a zero intercept. Numbers above trend-lines represent F_i values (Eq. 1).

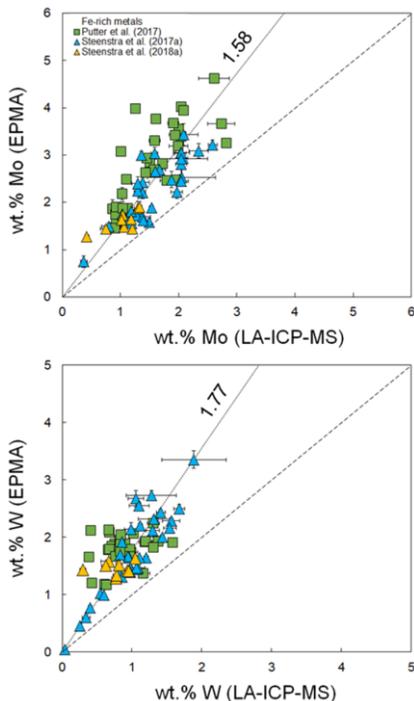


Fig. 2: Comparison between EPMA and LA-ICP-MS derived abundances of Mo and W. See Fig. 1 for details.

To quantify the matrix effects, we consider the fractionation index or F_i , which is defined as:

$$F_i = \frac{\text{reference concentration by weight of element } i \text{ in metal (EPMA)}}{\text{concentration by weight of element } i \text{ in metal (LA - ICP - MS)}} \quad (1)$$

The F_i values derived for the various elements for Fe-rich metals show an excellent correlation with their 50% condensation temperatures [12] (Fig. 3).

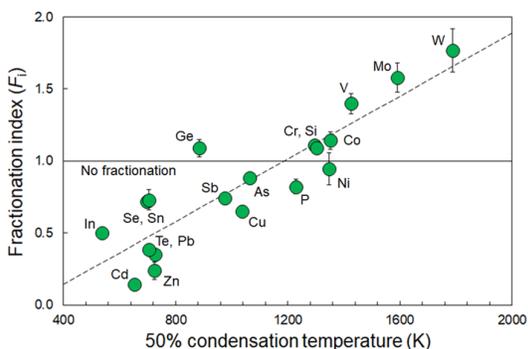


Fig. 3: F_i values versus the 50% condensation T [12]. Dashed line represents a linear fit to the data, which allows for calculation of F_i values for elements for which no data is presently available.

The F_i values derived in previous studies for both metals and sulfides [5,13-15] that were obtained using similar laser systems agree well with the values derived in this study (Fig. 4). Our new model also reproduces the F_i values derived for several HSE (Pd, Rh, Pt) in sulfides [5] within error. This strongly suggests that matrix effects are similar for sulfides and metals.

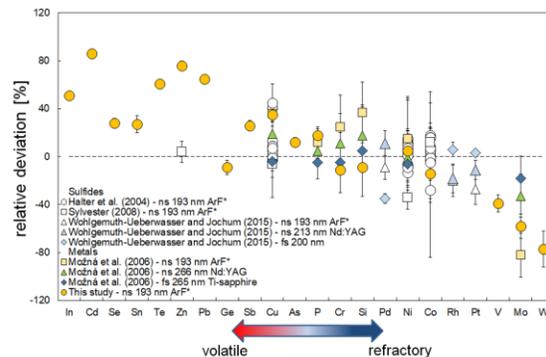


Fig. 4: Deviations of LA-ICP-MS data versus EPMA measurements as a function of elemental volatility. Also plotted are data from previous studies [5,13-15].

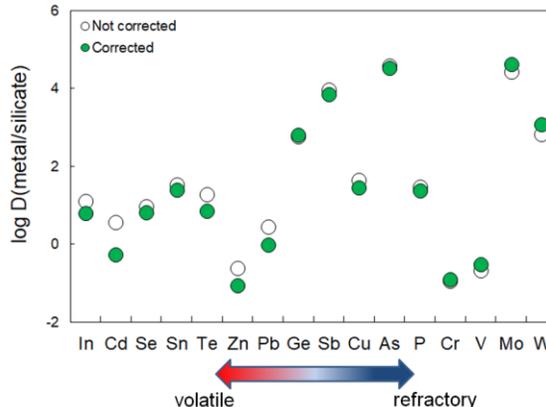


Fig. 5: The effect of matrix effects on D values.

Discussion: To illustrate the importance of addressing matrix effects in deriving metal-silicate partition coefficients (D 's), we plot in Fig. 5 corrected and uncorrected D values from [6,7] as a function of elemental volatility. The D values are overestimated for volatile elements by up to 0.85 log units if matrix effects are ignored. The D values for refractory elements may be underestimated by up to 0.25 log units. Failure to account for these effects will result in substantial inter-laboratory offsets of D values [16].

References: [1] Righter (2003) *Ann Rev Earth Plan Sci* 31 [2] Vaughan (2018) *Rev Min Geochem* 61 [3] Bouhifd et al (2013) *GCA* 114, 13 [4] Gourcerol et al (2018) *Min Dep* 53, 871 [5] Wohlgemuth & Ueberwasser (2015) *JAAS* 30, 2469 [6] Putter et al (2017) *LPSC* 48, 1055 [7] Seegers et al (2017) *LPSC* 48, 1053 [8] Steenstra et al (2018) *Icarus*, in press [9] Steenstra et al (2017) *GCA* 212, 62 [10] Steenstra et al (2017) *Sci. Rep.* 14552 [11] Steenstra et al (2018) *LPSC* 49, 1198 [12] Lodders (2003) *AJ* 591, 1220 [13] Halter et al (2004) *CBMP* 147, 385 [14] Sylvester et al (2008) *In: LA-ICP-MS in the Earth Sciences* 62 [15] Možná et al (2006) *JAAS* 21, 1194 [16] Steenstra et al (2018) *JAAS*, in press