Production of barium and light rare earth element oxides during LA-ICP-MS microanalysis

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Production rates of molecular oxides (M$^{16}$O$^-$/$M$\textsuperscript{+}) of Ba and light rare earth elements (LREE: La, Ce, Pr and Nd), have been measured by Laser Ablation ICP-MS (LA-ICP-MS) analysis via ablation of a Ba and LREE-doped synthetic silicate glass. Our work confirms that oxide production is related to the strength of the M–O bond in the MO$^-$ ion, and in agreement with solution-based measurements and theoretical considerations, M–O bond strength correlates linearly with log(MO$^-$/$M^{+}$). Oxide production is also strongly dependent on plasma conditions and increases markedly at higher nebulizer gas flow rates (and corresponding lower plasma temperatures), although relative differences between oxide production rates for Ba and LREE do not remain constant. Oxide production is also influenced by availability of oxygen within the plasma. Immediately after opening the ablation chamber to the atmosphere, oxide production rates can be 50–100% higher than those measured after the ablation chamber has been purged of atmospheric oxygen. Differences in plasma load related to differences in ablation rates appear to have little influence on oxide production. Calculations based on our data confirm that the widespread approach of tuning plasma conditions so that measured ThO$^-$/Th$^+$ ratios are less than a few percent is largely suitable for reducing isobaric interferences from Ba and LREE oxides on middle light rare earth element isotopes to levels suitable for trace element analysis for most geological materials. However contributions to Gd from LREE oxides may exceed analytical uncertainties in moderately to highly LREE-enriched materials ([La/Gd] \textsuperscript{H} < \sim 3). Contributions from BaO to Eu are only significant for materials with Ba/Eu ratios \textsuperscript{H} \gg 1000.

Introduction

In-situ chemical microanalysis using Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) is a powerful tool for the rapid analysis of the chemical and isotopic composition of solid materials at high spatial resolution, and as such has many applications in the earth, environmental and other sciences.\textsuperscript{1} One important limitation for LA-ICP-MS analysis, as well as for other ICP-MS-based techniques, are isobaric interferences caused by production of ionized molecular species within the plasma or ion extraction interface.\textsuperscript{2–7} Elements such as oxygen, hydrogen and argon are readily available, being derived either from the sample matrix, from the gas-handling systems and/or through entrainment of atmospheric gases by the plasma. Combination of these elements with each other, and with material from the analysed matrix results in production of a large range of molecular species, of which the most important are typically oxides, hydrides and argides.\textsuperscript{2}

Molecular oxides represent one concern for trace metal analyses of geological materials by many ICP-MS techniques. Many geological and other matrices contain a high proportion of oxygen and, in combination with oxygen contaminants in plasma gases and entrained into the plasma, provide ample opportunity for molecular oxide formation. Combination of $^{16}$O with an isotope of mass M produces a molecular ion (M$^{16}$O$^-$) at a mass that isobarically interferes with peaks equivalent in mass to M + 16 (we consider only monovalent species here). There are also M$^{17}$O$^-$ and M$^{18}$O$^-$ isobars, but the low abundances of $^{17}$O and $^{18}$O in natural materials (0.037 and 0.20%) reduces their importance, and from here on we use MO$^-$ to refer only to the M$^{16}$O$^-$ oxide ion. At a given mass the contribution from molecular oxides is a function of the rate at which the interfering oxide ion is produced, but is also strongly dependent on the relative abundances of the analyte isotope and the isotope that forms the interfering oxide, and thus may be strongly matrix and sample specific. For analysis of geological materials potentially troublesome examples include the interference of Ba and light rare earth elements (LREE) on middle rare earth elements (MREE) as well as MREE oxides on heavy rare earth elements (HREE), Re and W oxides on Hg, and HREE oxides on Re.\textsuperscript{5,6} Molecular oxides may be of particular concern for LA-ICP-MS analysis as sample material cannot be chemically treated prior to analysis to remove specific troublesome elements.

Oxide production rates for solution-based ICP-MS have been characterized by numerous previous studies (including ref. 2–4, 9–11 and many others). These demonstrate that molecular oxide formation is a function of both plasma and sampling conditions, as well as the strength of the M–O bond in the MO$^-$ ion, as expected from theoretical considerations (see below). This should also be the case for LA-ICP-MS analysis, however as yet there has been little direct characterization of oxide production during LA-ICP-MS. Jarvis \textit{et al.}\textsuperscript{2} reported representative oxide production rates for Ba, Ce, Th and U during ablation of a standard gel by a Nd:YAG laser that ranged between 0.0225 and 0.74%. However to date, the relationship of oxide production rates to plasma conditions and M–O bond strengths has not been studied in detail, nor has any exploration been made of any relation between oxide...
formation and ablation conditions. This may be important if differences in plasma particulate loading associated with variations in ablation conditions exert influence over oxide formation. Furthermore, oxide species are also known to form within the laser-induced plasmas formed during ablation, 12 and in cases where breakdown of ablated particulate within the plasma is incomplete, 13 could also conceivably contribute to MO$^+$.

In this contribution we investigate the rates of production of molecular oxides by Ba and LREE in a basaltic composition synthetic silicate glass during LA-ICP-MS analysis. Using techniques developed for secondary ion mass spectrometry (SIMS), another in situ analysis technique where molecular oxide ion production is well characterized, 14,15 we describe a method for measurement of oxide production rates using synthetic silicate glasses and use this to examine variations in oxide production rate in light of variations in M–O bond energy, plasma conditions and laser ablation conditions. We also discuss the limits that oxide production may place on analytical quality and evaluate methods for correcting isobaric oxide interferences.

Formation of MO$^+$ ions during ICP-MS analysis

Although inductively coupled plasmas are efficient ionization sources they also produce a range of polyatomic ion species, with argides (MAr$^+$), oxides (MO$^+$), hydroxides (MOH$^+$) and hydrides (MH$^+$) among the most common. 2,4,5,9 Although these may form both within the plasma and during ion extraction, it is clear that a significant number, and perhaps a large majority, of these ions form within the plasma itself. 16

Formation or dissociation of a metal oxide ion within the plasma occurs primarily by the reaction

$$\text{MO}^+ \leftrightarrow \text{M}^+ + \text{O}$$  

(1)

The dissociation constant for MO$^+$ is given by

$$K_d = \frac{n_{\text{M}^+}n_{\text{O}}}{n_{\text{MO}^+}}$$  

(2)

Where $n$ is the number density (atoms cm$^{-3}$) for each species. 16 $K_d$ is related to the temperature of the plasma gas ($T_{\text{gas}}$), the bond dissociation energy ($D_b$) for the MO$^+$ ion, the atomic or molecular weight ($M$) and the overall partition function ($Z$) for $\text{M}^+$, O and MO$^+$, by an equation similar to the Saha equation: 4,16

$$\log K_d = 1.5\log T_{\text{gas}} - 5040D_b/T_{\text{gas}} + \log(M_{\text{M}}M_{\text{O}}/M_{\text{MO}^+}) + \log(Z_{\text{M}}Z_{\text{O}}/Z_{\text{MO}^+}) + 20.274$$  

(3)

Calculation of exact MO$^+$ production using eqn (3) is complicated by the difficulty in evaluating $Z_{\text{MO}^+}$, which requires the full spectroscopic properties of MO$^+$ to be known. However, eqn (3) suggests that $\log(M_{\text{O}}/M_{\text{M}})$ should be proportional to the $M$–O bond strength within the MO$^+$ ion, and for a given element, inversely related to plasma temperature. This results in a strong relation between oxide formation rates measured from solution ICP-MS and parameters which govern plasma and sampling conditions, such as nebulizer gas flow rates, forward power, the distance between load coil and sampler, and sampler and skimmer orifice sizes. 2,3,10,17

Oxide production rates are also strongly influenced by availability of oxygen, and production rates of molecular oxides (as well as hydroxides and hydrides) are expected to be lower for LA-ICP-MS analysis using a dry plasma than for conventional solution-based ICP-MS analysis. 4,5 High loading of water-dominated aerosol in a wet plasma, which supplies O and H, and the large number of oxygen (and hydrogen) atoms available per analyte atom in dilute aqueous solutions promotes oxide formation. Reported ThO$^+/Th^+$ for wet plasma ICP-MS range from values that are similar to or slightly greater than those routinely used for LA-ICP-MS ($\leq 2.5\%^{10}$) to significantly greater values ($> 20\%^{11}$).

Strategies for control of molecular oxide interferences

For LA-ICP-MS the most common means of controlling oxide production is by tuning plasma conditions to reduce the measured oxide production for Th to below a threshold where oxide contributions are considered negligible (generally ThO$^+$/Th$^+ < \sim 2.5\%$). Monitoring of the ThO$^+/Th^+$ ratios is particularly useful for LA-ICP-MS as there is no naturally occurring isotope at the ThO$^+$ mass (248) and this ratio can thus be measured in any material that contains sufficient Th. By a happy coincidence the Th–O bond is among the strongest known for oxides (210 kcal mol$^{-1}$ 18) and thus ThO$^+/Th^+$ production rates should also represent the maximum oxide production rate expected for a given set of plasma conditions.

Technical solutions can also be applied to the amelioration of oxide interferences during laser ablation. Mason$^7$ reviewed application of collision and reaction cells to reduction of molecular interferences for LA-ICP-MS, including metal oxides and concluded that these could provide a substantial reduction in contributions from molecular species, albeit with some loss in sensitivity. 19 Sector field mass analysers also offer the possibility of resolving interfering oxides from monoisotopic species, although the high mass resolving power required for many applications (e.g. $> 7000$ for REE oxides) results in a corresponding marked decrease in transmission ($\sim 90\%$) and sensitivity. For LA-ICP-MS any change in measurement conditions that results in a reduction of sensitivity is a cause for concern as this will directly translate into increases in minimum detection limits and degradation of effective spatial resolution.

Correction schemes based on measured oxide production rates have also been used to account for oxide interferences during REE analysis by solution-based ICP-MS techniques. 2 Aries$^6$ and Raut$^6$ 11 detail schemes where ThO$^+/Th^+$ ratios measured on a sample by sample basis can be used to correct for molecular contributions to other peaks via measured relative production factors and the observation that measured (ThO$^+/Th^+$)/(MO$^+/M^+$) ratios remain constant over a range of analytical conditions. To date, relatively less effort has been made to directly measure oxide production rates and apply corrections on this basis for LA-ICP-MS analysis, although Sun$^8$ also used YbO$^+/Yb^+$ ratios measured directly on NIST 610 glass to correct for the interference of $^{121}$YbO$^+$ on $^{187}$Re$^+$. 20

Methods

Measurement of oxide production rates during LA-ICP-MS

Accurate measurement of oxide production rates during ICP-MS analysis requires that ion beams corresponding to both isotope M$^+$ and oxide MO$^+$ be free from other isobaric interferences. For solution based ICP-MS this is relatively easy to achieve through preparation of solutions containing elements so that they do not interfere with each other (e.g. ref. 10 and 11). For laser ablation this is more difficult, particularly for study of geological and other complex natural materials. The presence of a range of elements results in “reverse” isobaric interference of monatomic ions of naturally-occurring isotopes on MO$^+$ peaks, and largely prevents accurate measurement of oxide production ratios for most elements—particularly as MO$^+$ peaks may be relatively low intensity. It is only for heavier elements (i.e. Au, Hg, Tl, Pb, Bi, Th and U) that MO$^+$/M$^+$ may be measured directly, as natural isotopes that interfere with MO$^+$ are not present. This could be rectified by ablation of pure materials, but this would be difficult to do at ablation conditions similar to those used for routine analysis, and also raises concerns about contamination of instrumentation.
An alternate approach follows that used to measure oxide production rates during Secondary Ion Mass Spectrometry (SIMS) analysis. In this case MO/$M^+$ ratios are measured directly using trace element-doped synthetic silicate glasses of appropriate bulk composition. Preparation of glasses with compositions equivalent to natural silicate minerals and liquids is relatively straightforward. Concentrations of doped elements should be relatively high in order to maximize MO$^+$ ion beams and to minimize the effect of any small degree of contamination in starting materials. Dopant elements are chosen to avoid interference between oxides and monoisotopic ions. Unlike standard reference materials, glasses prepared for measurements of oxide production ratios do not require stringent characterization for concentration and homogeneity of trace element abundances, as all that is required for a given analysis is the determination of the MO/$M^+$ production ratio.

For this study we have used the latter approach to characterize the production of Ba and LREE (La, Ce, Pr, Nd) oxides during LA-ICP-MS analysis of a synthetic silicate glass of basaltic composition. This was originally prepared by W. F. McDonough and W. Hibben at the Research School of Earth Sciences, The Australian National University, for use with SIMS trace element studies and doped at nominal levels of 1000 μg g$^{-1}$ with Cs, Ba, La, Ce, Pr and Nd. For this study measurements were made using a VG ExCell quadrupole ICP-MS coupled with a NewWave DUV 193 nm ArF Excimer laser at Oregon State University. All ablations were conducted with He as the carrier gas at a flow rate of 0.75 l min$^{-1}$, and except where noted were only made after the sample had been in the ablation chamber and within the He flow for more than 60 minutes (see below). Measurements of MO/$M^+$ were made at Ar nebulizer gas flow rates between 0.9–1.05 l min$^{-1}$ and with a variety of ablation conditions, with a stationary laser spot ranging between 50–115 μm in diameter and pulse frequency from 2–15 Hz. For all analyses pulse energy remained broadly constant at 10–12 J cm$^{-2}$. Further details of typical analytical conditions used with this equipment may be found in ref. 21. An emphasis was placed on making measurements using ablation conditions similar to those used for routine trace element analysis in this laboratory, and this largely precluded measurement of $^{135}$BaO/$^{133}$Cs$^+$ as the low production rate of the $^{135}$Ba$^+$ ion beam was not consistently statistically resolvable (within six standard deviations above background). From this it can be inferred that $^{133}$CsO/$^{133}$Cs$^+$ was below 0.005% in all cases, consistent with the relatively low strength of the Cs–O bond (70 kcal mol$^{-1}$). In addition, $^{135}$BaO$^+$ and $^{138}$BaO$^+$ ion beams were also not always detectable and $^{138}$BaO$^+$ was also used to calculate oxide factors for Ba. For this determination, small corrections were made for interferences from $^{138}$La$^+$, $^{138}$Ce$^+$, $^{138}$LaO$^+$ and $^{138}$CeO$^+$. Overall, for the conditions used for this study contributions from $^{138}$Ce and $^{138}$La and their oxides resulted in ~1–2% increase in the measured $^{138}$BaO$^+$/$^{138}$Ba$^+$ ratio.

Our method also does not allow direct measurement of hydride and hydroxide production rates. However, assessment of hydride production rates at typical analysis conditions using $^{232}$Th showed that ThH$^+$/Th$^+$ and ThOH$^+$/Th$^+$ ratios were <0.005% and at higher nebulizer flow rates <0.01%. Jarvis et al. reported a BaOH$^+$/Ba$^+$ production rate of 0.015% for ablation of a standard gel. Overall at these production rates hydrides and hydroxides were unlikely to interfere significantly with measurement of oxide production rates.

Solution ICP-MS data reported herein were obtained on the same VG PQ ExCell instrument using a Glass Expansion concentric nebulizer and prepared 20 ng g$^{-1}$ solutions of Ba, La, Ce, U and Th in 1% HNO$_3$. Measurements were also made over a range of nebulizer flow rates (1.03–1.06 l min$^{-1}$, Ar). Hydride production rates were also measured for Ba and La and these were slightly higher than those measured for Th with LA-ICP-MS, but were still less than 0.01%. Hydroxide production rates measured for Ce from solution nebulization were <0.005%.

Results

Results from solution measurements are shown in Fig. 1. The results of a series of experiments measuring oxide production rates (MO/$M^+$ ratios) by LA-ICP-MS for $^{138}$Ba, $^{139}$La, $^{138}$Ba, $^{139}$La, $^{140}$Ce, $^{141}$Pr, $^{141}$Nd and $^{145}$Nd over a range of ablation and plasma conditions are shown in Fig. 2–8. As expected, measured MO/$M^+$ ratios from both sample introduction methods strongly correlate with both the M–O bond energy and with nebulizer flow rates (Fig. 1 and 3). Note that following previous workers we have used the M–O bond energy for the MO molecule, rather than the MO$^+$ ion.

For laser ablation the reproducibility of individual MO/$M^+$ measurements is largely dependent on the size of the MO$^+$ peak, which in turn is a function of both the ablation rate and MO/$M^+$ ratio. Comparison of MO/$M^+$ calculated from $^{143}$Nd and $^{142}$Nd show a reproducibility for NdO$^+$/Nd$^+$ of between 1–3% ($\sigma$) for the range of ablation conditions and nebulizer flow rates used. In a separate experiment three replicate analyses using a laser spot diameter of 50 μm, 4 Hz pulse frequency, and tuning conditions similar to those used for routine analysis (nebulizer flow rate = 0.90 l min$^{-1}$) showed standard deviations of 20%, 12%, 9% 11%, 10%, 6% and 18% respectively for $^{138}$Ba, $^{137}$Ba, $^{138}$La, $^{140}$Ce, $^{141}$Pr, $^{142}$Nd and $^{145}$Nd, and these are probably broadly representative of the uncertainties in MO/$M^+$ ratios during routine analysis.

Discussion

Variations in oxide production with oxide bond energy, plasma conditions and ablation parameters

Our experiments demonstrate that Ba and LREE oxide production rates during LA-ICP-MS are primarily a function of three factors: (i) availability of oxygen within the gas handling system; (ii) the strength of the M–O bond in the MO$^+$ ion; and (iii) conditions within the plasma. The effect of the latter two...
has been widely demonstrated for solution-based ICP-MS and we have confirmed that it is also the case for the solution nebulization sample introduction system used in this study (Fig. 1).

The effect of oxygen availability on oxide formation during LA-ICP-MS is shown by the strong relationship observed between the length of time since closing the ablation chamber (after opening it to atmospheric oxygen) and measured oxide production rates. Fig. 2 shows that measured $\text{MO}^+ / \text{M}^+$ ratios for $^{139}\text{La}$, $^{140}\text{Ce}$, $^{143}\text{Nd}$ and $^{145}\text{Nd}$ decrease rapidly after closing the ablation chamber (and setting the He carrier gas flow rate to 0.75 l min$^{-1}$), and overall oxide production rates for these REE decrease by 50–100% until stabilising after ~60–90 minutes. This observation infers that oxygen trapped within the chamber contributes significantly to oxide production until it is gradually purged from the chamber by continual He flow. After this time sources of oxygen for oxide production are probably largely confined to oxygen either derived from the sample matrix, present as impurities in the gas handling system and/or entrained by the plasma. Thus one simple means to reduce oxide formation is to wait sufficient time after sample changes to allow trapped oxygen to be purged from the ablation chamber, and/or to minimize the amount of contaminant oxygen within the gas handling system. Modifications of ablation chamber design may also help to limit the amount of oxygen trapped within the ablation chamber and increase the rate at which it is purged from the chamber.

Our data also demonstrate the inter-relationship between oxide production, MO$^+$ dissociation energy and plasma conditions during LA-ICP-MS analysis. In Fig. 3A we compare the MO$^+$ dissociation energy with measured log($\text{MO}^+ / \text{M}^+$). Data are shown for four different Ar nebulizer gas flow rates, with 0.90 l min$^{-1}$ representing plasma conditions similar to those used for routine quantitative LA-ICP-MS analysis of silicate glasses and minerals in this laboratory. Although they were not measured directly during analysis at these conditions, Th oxide production rates at this flow rate (ThO$^+ / \text{Th}^+$) were determined to be ≤2.5% by analysis of NIST 612 glass prior to analysis, consistent with standard tuning protocol for this instrument. All data were also recorded under identical ablation conditions, using a laser spot size of 70 μm, pulse rate of 4 Hz, and laser energy of ~12 J cm$^{-2}$ per pulse.

As expected from eqn (3), at a given nebulizer flow rate, log($\text{MO}^+ / \text{M}^+$) correlates linearly with $\text{M}$–$\text{O}$ bond energy, with correlation coefficients greater than $r = 0.97$. This confirms that this relationship, previously recognized for solution nebulization analyses (e.g. Fig. 1) is also the case for LA-ICP-MS, and implies that the majority of oxide formation during LA-ICP-MS occurs within the plasma or interface of the ICP-MS (e.g. ref. 4). Oxide production rates also increase systematically at higher nebulizer gas flow rates. In Fig. 3A the correlations between $\text{M}$–$\text{O}$ bond energy and log($\text{MO}^+ / \text{M}^+$) are displaced to progressively higher oxide production ratios with increasing nebulizer flow, and this variation is shown in more detail in Fig. 3B. At flow rates of 1.05 l min$^{-1}$ Ar, MO$^+ / \text{M}^+$ ratios for Ba, La, Pr, Ce and Nd were factors of ~30, 45, 86, 60 and 25 greater than those at 0.90 l min$^{-1}$.

Fig. 4 shows measured MO$^+ / \text{M}^+$ ratios over a range of laser spot diameters and pulse rates. Over the range of these conditions (2–15 Hz pulse frequency and 50–115 μm spot diameter) there appears there is little consistent variation in measured MO$^+ / \text{M}^+$ with changes in either pulse rate or spot diameter.

An additional interesting observation is that the relative rate of oxide formation for Ba and REE also changes with nebulizer gas flow rates. This is in contrast to observations from solution nebulization measurements, where the ratio of MO$^+ / \text{M}^+$ measured for REE and for Th have been reported to remain constant over a wide range of plasma conditions.10 Fig. 5A shows measured oxide production rates for LA-ICP-MS double-normalized to oxide production rates for $^{139}\text{La}$ and production for each isotope measured at nebulizer flow rates of 0.85 l min$^{-1}$ Ar. Large changes are observed in relative oxide production rates of all elements studied. In particular Ce shows reverse behaviour to Pr and La in that oxide production relative to La increases at nebulizer flow rates above 0.95 l min$^{-1}$. The cause of this difference is at present unknown, but may relate to oxidative reactions involving Ce within the laser-induced plasma (e.g. ref. 12 and 22)—although overall the strong relation observed between plasma conditions and oxide production rates, together with the lack of clear relation.
between ablation conditions and oxide production suggests that oxide production within the laser-induced plasma at the site of ablation has relatively little effect on the ultimate oxide production rates. We also note that normalized oxide production rates measured using solution nebulization for this study also vary significantly with changes in nebulizer flow rate (Fig. 5B), and that the anomalous behaviour of Ce is not apparent. The changes in relative production rates of REEO$^+$ preclude direct application of the correction scheme of Aries et al. $^{10}$ or Raut et al. $^{11}$ to LA-ICP-MS analysis in this instrument as these rely on constant rates of REEO$^+/$REE$^+$ production relative to that of ThO$^+/$/Th$^+$. 

Effects of BaO$^+$ and LREEO$^+$ on MREE measurements in silicate glasses

One issue during analysis of REE by many mass spectrometric techniques, including ICP-MS analysis, is the isobaric interference of Ba and LREE oxides on the isotopes of the MREE (Eu, Gd, Dy, Tm and Ho). In many natural materials these interferences are exacerbated by the relatively high abundances of Ba relative to Eu, and of La, Ce and Pr relative to Gd, Tb, Dy and Ho. To investigate this further for LA-ICP-MS we have used measured oxide production rates to calculate oxide contributions to MREE isotopes from oxides for three common reference glass compositions (BCR-2G, BHVO-2G, T1-G) and Durango apatite. Collectively these represent a broad range of Ba/Eu ratios and LREE enrichment. Calculations are based on oxide production rates measured during typical routine analysis conditions (i.e. tuning conditions optimized to produce ThO$^+/$/Th$^+ \leq 2.5\%$), resulting in MO$^+/$/M$^+$ ratios for Ba, La, Ce, Pr and Nd of 0.04, 2.08, 1.32, 0.74, and 0.4%.

![Fig. 4](image-url) Measured oxide production for LREE with changing (A) laser pulse rate, and (B) spot diameter.

![Fig. 5](image-url) Normalized (MO$^+/$/M$^+$)(139LaO$^+/$/139La$^+$) as a function of nebulizer flow rate for (A) LA-ICP-MS and (B) solution nebulization analyses. Measured (MO$^+/$/M$^+$)(139LaO$^+/$/139La$^+$) have been normalized to those obtained at nebulizer flow rates of 0.85 and 1.03 l min$^{-1}$ Ar for LA-ICP-MS and solution nebulization measurements respectively.

![Fig. 6](image-url) Calculated contributions to MREE ion beams from Ba and LREE oxides during LA-ICP-MS analysis for four different compositions: (A) BHVO-2G, (B) BCR-2G, (C) T1-G and (D) Durango apatite. REE compositions of these materials are from Jochum et al. $^{24}$, Kent et al. $^{25}$ and Hutcheon. $^{26}$ Further details of the calculations are given in the text. Grey boxes show level where oxide interference will become apparent over other analytical errors.
interferences that exceed 10% in materials with relatively low \([\text{La/Gd}]\) ratios (following convention the subscript \(N\) refers to the La/Gd ratio normalized to that in bulk silicate earth where \(\text{La/Gd} = 1.204\)) \(^{155}\)Gd is somewhat better as \(\text{PrO}^+/\text{Pr}^-\) production is lower and for natural materials Pr abundances are lower than for La and Ce, and \(^{155}\)Gd is the most commonly used Gd isotope for concentration measurements. However, this isotope can still have interference from \(^{149}\)PrO at the level of 5–10% in natural materials with \([\text{La/Gd}]_N > 3\) (Fig. 7), which include many materials with naturally LREE-enriched compositions. Interference of Ba oxides on Eu appears to be of minimal concern, despite the higher abundances of Ba over Eu in many natural materials. The low oxide production rates for Ba limit significant interferences to materials with exceptionally high Ba/Eu ratios (\(\gg 1000\); Fig. 8), and thus is significant in a more limited number of matrices.

Overall these calculations confirm that following a protocol whereby plasma conditions are optimized to ensure measured \(\text{ThO}^+/\text{Th}^-\) is below \(\sim 2.5\%\) is generally adequate to ensure that contributions from Ba and LREE oxides to MREE are not significant in a broad range of compositions, with the exception of Gd measurements in LREE enriched samples. However in situations where oxide production is of concern, direct measurement of oxide production rates, using the techniques outlined herein and measured at identical plasma tuning conditions will allow oxide contributions to specific mono-isotopic peaks to be determined and corrected.

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References