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**AN EXPERIMENTAL STUDY OF THE BEHAVIOUR OF
CERIUM/MOLYBDENUM RATIOS DURING SUBDUCTION: IMPLICATIONS
FOR TRACING THE SLAB COMPONENT IN THE LESSER ANTILLES AND
MARIANA ARC**

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27
28 **ABSTRACT**

29 Arc magmas are very distinct in their geochemical signatures, a consequence of trace
30 element enriched components from the subducting slab that are incorporated into melts of the
31 overlying mantle wedge. However, it is not always straightforward to distinguish such slab
32 components from assimilation of crustal rocks during subsequent differentiation, given that
33 both reservoirs can share similar geochemical characteristics. This has prompted the
34 development of new tools, such as $^{98}\text{Mo}/^{95}\text{Mo}$ analyses used in combination with Ce/Mo
35 measurements. The diverse range of $\delta^{98/95}\text{Mo}$ in the surface environment gives rise to variable
36 isotopic compositions of subducted Mo. Most diagnostic of these is the extremely isotopically
37 heavy Mo in marine black shales, such as those drilled in the vicinity of the Lesser Antilles.
38 However, subducting assemblages are invariably complex and differing melting behaviours
39 and contrasting $\delta^{98/95}\text{Mo}$ of various crustal components may counter-balance one another,
40 requiring a more detailed investigation of the behaviour of Mo and Ce in the down-going slab.

41 This study is dedicated to identifying possible hosts for Mo and Ce in sediments and
42 basalt at sub-arc depths. New melting experiments were performed (3 GPa, 800–900°C),
43 using synthetic carbon-rich black shale and calcareous sediment compositions from the Lesser
44 Antilles arc. In addition, new analyses of Mo concentrations and Ce/Mo data of previously
45 published partial melting studies on altered oceanic crust and volcanoclastics (Mariana Arc)
46 are presented. Our study suggests that sulfide and to a lesser extent rutile are the major hosts
47 for Mo in eclogites, whereas the presence or absence of monazite (Ca-poor sediments),
48 epidote (Ca-rich sediments) and carbonate (CaCO_3 -rich sediments) controls Ce concentrations
49 in carbonaceous sediments. Redox conditions are found to be of great importance for the
50 Ce/Mo ratios of slab components derived from these lithologies because of their influence on
51 sulfide and epidote stability. It is further shown that rutile only hosts Mo at suitably reducing
52 conditions, in concordance with previous studies. The combination of measured Ce/Mo with

our experimental results thus places important constraints on phase petrology and redox conditions in the subducted slab.

1. INTRODUCTION

1.1 The Lesser Antilles and Mariana Arc systems

Subduction zone magmas acquire their distinctive geochemical signatures either from fluids/melts released from the descending slab (e.g. Gill, 1981) or buoyant portions of the slab itself that rise into the mantle wedge (e.g. Gerya & Yuen 2003). In either case, slab-derived materials (fluids, melts, diapirs) transfer components that are “exotic” (with respect to the mantle) into the source regions of volcanic arcs (e.g. Lesser Antilles Arc, Fig. 1a; Mariana Arc, Fig. 1b). Although there is a range of tracers available for studying this process (e.g. Tera et al., 1986; McCulloch and Gamble, 1991; Gill, 1981; Hawkesworth et al., 1991; Elliott, 2003), there are many field examples where it is difficult to distinguish a slab component from assimilation of crustal rocks during subsequent differentiation. A prime example is in the Lesser Antilles (Davidson et al., 1987) (Fig. 1a), where overlying crust and subducted slab share similar isotopic compositions and trace element characters.

The importance of slab addition versus crustal contamination in the Lesser Antilles remains hotly debated (e.g. Thirlwall and Graham, 1984; White and Dupré, 1986; Davidson, 1987; Smith et al., 1996; Turner et al., 1996; Van Soest et al., 2002; Bouvier et al., 2008; Labanieh et al., 2012; Bezard et al., 2015). Prominent along-arc geochemical variations in trace element and isotope ratios correlate with changes in subducting sediment characteristics (south: >>1000 m thick, dominantly terrigenous sediments; north: <300 m thick, marine and terrigenous sediments) (e.g. Tucholke et al., 1982; White et al., 1985; Westbrook et al., 1988; Plank and Langmuir, 1988). Notably, the lavas in the southern Lesser Antilles exhibit some of the most radiogenic Pb isotopic compositions found in intra-ocean island arcs worldwide (e.g. White and Dupré, 1986). That some of these lavas are more radiogenic than the sediments drilled in DSDP leg 78 Site 543, east of Dominica (Fig. 1a), has become one of the principal

arguments in favour of crustal contamination (e.g. [Thirlwall et al., 1996](#)). On the other hand, [Carpentier et al. \(2008\)](#) hypothesized that the “yet-to-be-subducted” sediments drilled in DSDP leg 78 Site 543 are much too young to be representative of the sediments that provide the southernmost arc with its current isotopic signature. [Carpentier et al. \(2008\)](#) investigated DSDP leg 14 Site 144, at the edge of the Dermerara Rise, a shallow submarine plateau consisting of older, carbonate-rich sediments off the coast of Surinam/French Guyana. They identified a carbonate-rich, black shale layer that is able to account for the entire Pb isotopic range found in the Lesser Antilles arc, provided that the anoxic event responsible for the black shales is a widespread feature in this part of the western Atlantic in the geological past.

A valuable test of the [Carpentier et al. \(2008\)](#) model is provided by the Mo isotope system. The high Mo concentrations of Atlantic black shales (59 $\mu\text{g/g}$, [Brumsack, 1980](#)) are much greater than other subducting lithologies (0.1–2 $\mu\text{g/g}$ Mo: e.g. [Freymuth et al., 2015](#)). Thus, any black shale component should dominate the Mo isotope budget of arc lavas. Moreover, black shales have diagnostic, elevated $\delta^{98/95}\text{Mo}_{\text{NIST 3134}}$ (Fig. 2a), where $\delta^{98/95}\text{Mo}_{\text{NIST 3134}}$ (hereafter abbreviated to $\delta^{98/95}\text{Mo}$ for convenience) is the relative difference in $^{98}\text{Mo}/^{95}\text{Mo}$ of the sample and National Institute of Standards and Technology, Standard Reference Material 3134 (NIST SRM 3134). In a companion study, we showed that $\delta^{98/95}\text{Mo}$ measurements provide a clear indicator of a black shale component in the source regions of primitive Lesser Antilles arc magmas ([Freymuth et al., 2016](#)). The southern islands of the Lesser Antilles are characterized by high Ce/Mo and high $\delta^{98/95}\text{Mo}$ values (LA2 in Fig. 2b). Isotopically, this is well explained by involvement of black shales ([Freymuth et al., 2016](#)), but the cause of high Ce/Mo ratios, rather than anticipated low values for a Mo-rich black shale component remains puzzling. Lavas from the rest of the arc form an array towards lower $\delta^{98/95}\text{Mo}$ and Ce/Mo (LA1 in Fig. 2b), consistent with a Mo-rich fluid derived from the mafic oceanic crust. The Ce/Mo ratio has been shown to be near constant in mid-ocean ridge and ocean island basalts, indicating comparable incompatibility of these two elements during

mantle melting (e.g. [Newsom et al., 1986](#)), but the markedly low Ce/Mo of some arc lavas (Fig 2b) can be explained by the mobility of Mo in slab-derived fluids ([Bali et al., 2012](#)).

Additional perspective on the behaviour of Mo in the Lesser Antilles is provided by results from the Mariana(-Izu-Bonin) arc system in the western Pacific ([Freymuth et al., 2015](#)). The location of this archetypical island arc means its lavas are considered to be free of crustal contamination by continental material, and provide a prime case for studying the effects of variable fluid/melt addition from the slab to the mantle wedge (see review by [Stern et al., 2003](#)). Subducting sediments in this arc are comprised of several lithologies (Fig. 1b) but the budgets of many key trace elements are dominated by layers of pelagic clay and volcanoclastics (e.g. [Larson et al., 1992](#)). Empirically, the isotopic array of the arc magmas is best reproduced using a sediment end-member that resembles volcanoclastics only (e.g. [Tollstrup and Gill, 2005](#); [Avanzinelli et al., 2012](#); [Prytulak et al., 2013](#)). [Freymuth et al. \(2015\)](#) suggest that the $\delta^{98/95}\text{Mo}$ composition of the Mariana lavas dominantly reflect addition of fluids/melts derived from mafic oceanic crust but fractionated to somewhat isotopically heavier values (M1 in Fig 2a), with only a subordinate influence of a variable, isotopically light sediment melt component (M2 in Fig. 2b).

The transport of Mo and Ce from slab to wedge strongly depends on their partitioning between fluids or melts and residual solids in the subducting slab¹. This behaviour is currently poorly characterised for Mo in general, and for Ce in the Lesser Antilles subducting lithologies in particular. This study therefore is dedicated to identifying possible hosts for Mo and Ce in various subducted lithologies. New experimental data on the melting behaviour of carbonate-rich black shales and other calcareous sediments similar to those found in DSDP

¹ Although we mostly refer to “melt”, all considerations are equally valid for sub-solidus fluids, provided account is taken of differences in the partitioning behaviour and accessory phase solubilities in low temperature, fluid-dominated environments. In both Marianas and Lesser Antilles, we identify two distinct slab-derived components which transport different combinations of elements, which we loosely refer to as “melt” and “fluid” in concordance with older studies.

leg 14 Site 144 are presented, which place constraints on the phase petrology of these sediments at variable redox conditions. We further present trace element analyses of experimental run products, including new analyses of Mo abundances and Ce/Mo from previously published partial melting studies (volcaniclastics from the Mariana arc: [Martindale et al., 2013](#); altered oceanic crust (AOC) from the mid-Atlantic ridge: [Carter et al., 2015](#)). In combination, the new data are used to reconcile the contrasting Ce/Mo patterns found in the Lesser Antilles and Mariana Arc and the controls on the Mo isotopic budget of these subduction zones.

1.2 The geochemistry of Molybdenum

Molybdenum is a transition metal that can occur in several redox states; most important in nature are Mo^{4+} and Mo^{6+} . Although Mo has previously been argued to be largely ‘immobile’ in subduction zone fluids ([Noll et al., 1996](#)), several recent studies ([König et al., 2009](#); [Freymuth et al., 2015](#)) have documented the opposite, suggesting its presence as a soluble, oxidised molybdate species (e.g. Mo^{6+} as MoO_4^{2-}). In general, Mo is known to readily partition into sulfides, and forms a stable sulfide phase, molybdenite (Mo^{4+} as MoS_2). Sulfides, in turn, are abundant in black shales (e.g. [Helz et al., 1996](#)) suggesting that there is a genetic link between the abundance of sulfides, oxygen-deficient conditions and Mo enrichment in euxinic sediments, although the exact processes for Mo scavenging are relatively complex (e.g. [Helz et al., 1996](#)). Some Mo can also be bound in the non-pyrite matrix (e.g. [Chappaz et al., 2013](#)). Where oxygen penetrates into euxinic sediments, Mo is remobilised quite efficiently via redox reactions (e.g. [Morford and Emerson, 1999](#)).

The solid-state equilibrium $\text{MoO}_2 + \frac{1}{2} \text{O}_2 = \text{MoO}_3$ lies 6.3 log units above the nickel-bunsenite (NNO) buffer (at 1000K, 0.1 MPa). The transition of Mo^{4+} and Mo^{6+} in melts and fluids, however, is displaced to much lower $f\text{O}_2$. According to [O'Neill and Eggins \(2002\)](#) the Mo^{4+} to Mo^{6+} transition is very sensitive to melt chemistry, but in synthetic iron-free melts it occurs in the vicinity of NNO-4(± 1) log units. In aqueous fluids at 2.6 GPa, 1000°C, [Bali et](#)

al. (2012) suggest that this transition occurs at slightly higher fO_2 (~NNO-1). As oxidation of Mo^{4+} to Mo^{6+} involves two electrons, the transition will be spread out over ~ 4 log units in fO_2 space regardless of the exact fO_2 at which it occurs. This range is less than that of Fe^{2+} to Fe^{3+} (one electron; > 8 log units) but more than S^{2-} (e.g. pyrrhotite, chalcopyrite) or S^- (e.g. pyrite) to S^{6+} (7–8 electrons; ~ 1 log unit). The latter transition occurs in melts above NNO at 3 GPa (e.g. Prouteau and Scaillet, 2013), but is known to be pressure-sensitive (Matjuschkin et al., 2016). Combined, these observations suggest that Mo is best mobilized in oxidising conditions where the majority of Mo is present as Mo^{6+} , which also destabilizes its sulfide host (see also König et al., 2010).

2. METHODS

2.1 Starting materials

We used synthetic starting materials mimicking sediments that have been drilled in the vicinity of the Lesser Antilles. In DSDP Leg 14 Site 144, sediments are always calcareous, and can be described as marls with varying proportions of clay and carbonate (Figs. 1a and 3) (e.g. Hayes et al., 1972, Carpentier et al., 2008). Sediments from DSDP Leg 78 Site 543 are predominantly marine clays with various proportions of continental (terrigenous) detritus (e.g. Biju-Duval et al., 1984, Carpentier et al., 2008). Sediments from this site are mostly carbonate-free, with the exception of a very small layer just above the mafic, igneous crust (Figs. 1a and 3).

Starting composition BS is designed to approximate a SiO_2 -rich black shale (144-27) that was analysed in our companion study (Freymuth et al., 2016). Chemical compositions of all starting mixes as well as some representative examples of natural sediments are summarized in Table 1. The BS composition is a mechanical mixture of pre-dried or fired synthetic oxides, apatite, fayalite, carbonate and natural albite. Approximately 2.7 wt% of gypsum ($CaSO_4 \cdot 2H_2O$) was added to the BS starting mix in order to ensure oxidising conditions. The effect of a residual sulfide is investigated by further adding FeS to selected

runs (Table 2). Trace elements were added to the homogenized starting mix by using nitric acid-based ICP-MS standard solutions. The trace element-bearing mixture was then dried under a heat lamp, before it was further homogenized in an agate mortar and denitrified at 450°C for 1 h.

Starting composition AS is designed to reflect the average leg 14 sediment prior to dilution by various proportions of CaCO₃. To that end, a carbon-free AS composition was first synthesized in the same way as described above, except that gypsum was not added. Trace element bearing AS was then mixed with 50 and 10 wt% of CaCO₃ (=AS1 and AS2 respectively) and re-homogenized. Additional Ba, Sr, and U were added to AS1 such that this composition would again lie close to that of black shales, but due to the absence of gypsum in this composition, reducing conditions were simulated in certain AS run products. The effect of residual sulfide and rutile is investigated by adding FeS₂ and TiO₂ respectively to selected runs (Table 2). Note that we have decided to use both FeS and FeS₂ as sulfide source, as either of these sulfides might be stable at run conditions, possibly inhibiting Mo equilibration if its diffusion in sulfides were slow. In contrast, it is to be expected that Mo equilibrates more readily with a sulfide phase if it is forced to change its composition and crystal structure. Natural black shales may further contain significant graphitic carbon. Graphite was not added to our synthetic starting material after initial tests with natural organic-rich (graphite-bearing) black shales yielded experimental run products with equilibration issues and textures that prevented *in-situ* analyses. The addition of graphite would have also acted as redox buffer, which was not intended for the purpose of this study (see also chapter 2.3). We acknowledge that the presence of significant carbon may influence the mobility of Mo, but this needs to be evaluated in a separate study.

Trace element concentration abundances in our experimental starting materials are designed to reflect nature (see Table 1), which has the advantage that measured concentrations and trace element ratios can be directly applied to natural systems. The only

exception is Mo in starting material AS2 (=average calcareous sediment of DSDP leg 14 Site 144), which contains approximately 31 $\mu\text{g/g}$ Mo. The average Mo concentrations of normal, “oxic” oceanic sediments are only on the order of 1 $\mu\text{g/g}$ (Freymuth et al., 2015, 2016). Because it can be difficult to accurately determine Mo at sub- $\mu\text{g/g}$ levels using ICP-MS, Mo was doped in this single case. The Ce/Mo ratio of the source material is an important factor influencing Ce/Mo of equilibrated fluids/melts, if the elements are not buffered by a solid phase. For results from experiments using the Mo-enriched AS2 starting composition, we therefore extrapolate to natural concentrations in the discussion section. All other starting materials mimic natural Ce/Mo, hence the results from experiments using these compositions will be directly applicable to nature.

2.2 Experiments

The powdered starting material was loaded together with approximately 15 wt% of distilled H_2O into Au capsules, which were then welded shut using a PUK microwelder. Potential H_2O -loss during welding is monitored by weighing the H_2O -bearing capsules before and after welding. Experiments were carried out in a $\frac{1}{2}$ -inch, end-loaded piston-cylinder at ETH Zürich. The pressure cell consisted of inner spacers of MgO or BN, a graphite furnace, and an outer sleeve of talc and Pyrex. A friction correction of 10% was applied (McDade et al., 2002). Temperatures were measured using a Pt₉₄/Rh₆-Pt₇₀/Rh₃₀ (“B-type”) thermocouple, inserted axially into the assembly. The pressure was kept constant at 3 GPa using an automatic pressure controller. The investigated temperature interval, 800–900°C, overlaps the range of recent thermal models of slab-top temperatures beneath the Lesser Antilles (760–800°C at a depth of ~120 km: Syracuse and Abers, 2006; Syracuse et al., 2010). Details of all runs can be found in Table 2. Experiments were quenched by turning off the power; cooling to below 200°C occurred in <10 s.

2.3 Redox conditions

The geochemistry of Mo suggests that redox conditions are important for understanding its behaviour. Unfortunately, it is not straightforward to buffer the $f\text{O}_2$ in solid-media experimental apparatus, especially in water-bearing systems and in the presence of other volatiles. Water loss via diffusion of H_2 through the capsule wall is a common feature of hydrous experiments (e.g. [Hall et al., 2004](#)), which can also lead to a net oxidation of Fe. Due to the very low molecular weight of hydrogen, a very small fraction of the bulk H_2O (<1 wt%) should suffice to oxidise all Fe^{2+} present in the starting material. It is therefore not possible to track such redox reactions by mass balances. Sulfur (and carbon) can also occur in oxidised or reduced species in piston cylinder experiments, which adds to the complexity of possible redox reactions in our experimental run products. Likewise, the oxidation of 1 mol of sulfate (S^{6+}) to 1 mol of sulfide (S^{2-}) can oxidise 7–8 mol of Fe, which is also not easy to track experimentally.

There is no consensus as to what controls the redox conditions in piston cylinder experiments in the absence of a solid buffer. Some studies suggest that the furnace assembly imposes a certain $f\text{O}_2$ (e.g. [Truckenbrodt et al., 1997](#); [Prouteau and Scaillet, 2013](#)), although most furnace assemblies cannot buffer an experiment to a constant $f\text{O}_2$. Nevertheless, these studies suggest that $f\text{O}_2$ should be at or above NNO for the furnace assembly (talc-pyrex-MgO/BN) and P-T-time conditions that we have used. Other studies argue that if negligible water is lost to the assembly and Fe can be prevented from alloying with the capsule wall, then the redox condition is simply a function of the bulk rock's initial $\text{Fe}^{3+}/\text{Fe}^{\text{tot}}$ ratio (e.g. [Kagi et al., 2005](#)). It is important to note that no initial ferric iron component is present in our bulk starting material, such that all changes in $\text{Fe}^{3+}/\text{Fe}^{\text{tot}}$ must be ascribed to redox reactions involving H_2 loss or sulfide/sulfate redox reactions (significant alloying of Fe with Au at these low temperatures is unlikely).

The redox conditions at which melting occurs in the different slab lithologies in nature are also not well constrained. One possibility is that the different slab units have little

opportunity to change their initial redox states, but it is equally possible that they interact with oxidising fluids or other redox-sensitive species during their descent. Anoxic sediments contain abundant graphite and sulfides that are indicative of reducing conditions and it is clear that their redox potential must be exhausted before black shale units can melt at oxidising conditions. Whether this is possible or not cannot be evaluated here. Rather than conducting experiments in the stability field of graphite, we have decided not to buffer the experiments, as we aim to get a first order idea on the behaviour of Mo during sediment melting at different redox conditions, that can later be extrapolated to various natural scenarios. The prevailing redox conditions, which vary in our experiments, can be tracked qualitatively via changes in the phase petrology and phase chemistry (discussed below). The geochemical behaviour of Mo implies that it is best mobilized at oxidising conditions (as Mo^{6+}); the fact that Mo can be mobilized from the subducted slab is documented in the studies of [König et al. \(2010\)](#) and [Freymuth et al. \(2015\)](#). It appears that the furnace assembly in which our H_2O -rich experiments are contained favours oxidising conditions at or above NNO. Additional use of sulfate in the starting materials further ensures oxidising conditions. The lack of sulfate in AS experiments, in turn, led to some experiments that have experienced significantly more reduced conditions, which implies a certain bulk rock control on $f\text{O}_2$ (discussed in more detail in section 4.1).

2.4 Analytical Methods

Run products were mounted and polished, and imaged by SEM. Compositions of silicates, carbonates, sulfides and glasses were determined using a JEOL 8200 superprobe at ETH Zürich. The accelerating voltage was set at 15 kV, whereas reference materials, currents, spot sizes and acquisition times were varied depending on the application: silicates and sulfides were measured with a focussed spot size and a beam current of 15 nA; acquisition times on peak and background were 30 and 15 s respectively. Glasses were measured with a 10 μm spot and 4 nA beam current; acquisition times were similar to minerals except for Na,

which was measured first for 10 and 5 s (peak and background). Carbonates were also measured with a reduced beam current (4 nA) and a defocussed spot (10 μm), but acquisition times on peak and background were increased to 60 and 30s. Molybdenum in rutile was quantified with an accelerating voltage of 20 kV, a 5 μm diameter, 50 nA electron beam and prolonged counting times (300s peak and 150s background), with counts being collected simultaneously on 2 crystals. Titanium, Fe and Al were fixed for ZAF corrections, and Na was measured as a means of detecting contamination. The accuracy of the individual calibrations was checked against secondary reference materials.

Trace elements in most glasses were measured by laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at ETH Zürich, using a Resonetics excimer laser (193 nm) coupled to a Thermo Element 2 ICP-MS. The following settings were applied: spot size 30 μm ; frequency 5 Hz; fluence 3.5 J/cm²; acquisition time 30 s (blank) and 40 s (peak); reference materials were NIST SRM 612 (external) SiO₂ or CaO (internal), and GSD-1G (secondary). Data were reduced using the Sills software ([Guillong et al., 2008](#)), and mineral inclusions were identified and excluded from the glass data via inspection of a count-rate versus time diagram. Trace elements of a sub-set of samples, and especially those with small melt pools or low Mo concentrations, were measured using the Cameca IMS-4f ion microprobe at the University of Edinburgh. The following settings were applied: 14.5 kV primary beam (O⁻ ions); 4.5 keV secondary beam; ~5 nA beam current; ~15–20 μm beam diameter; 75±20 V energy filter. For reasons detailed in [Skora and Blundy \(2012\)](#), we constructed working curves for all trace elements, based on a range of MPI-DING (ATHO, STH5, T1, ML3, GOR: [Jochum et al., 2000](#)) and USGS glass reference materials (GSD, BCR, BIR, BHVO), and ratioed against ³⁰Si. The suite of reference materials was supplemented with a self-made reference material, a supra-liquidus run of a diluted BS composition (20% BS + 80% albite + 10 wt% H₂O). The dilution is necessary so that the high CO₂ content of this bulk composition could be fully homogenised and quenched to vesicle-free glass. A

second reference material used the same diluted composition but was additionally doped with >100 µg/g Mo. Gravimetric compositions of the diluted BS glass were verified using EMPA and LA-ICP-MS.

3. RESULTS

3.1 General observations

Phase proportions in all experiments were obtained by unweighted least squares regression, using volatile-free compositions (Table 2). Phases that occur in trace amounts (< ~1-2 vol%) were excluded. For reasons detailed in [Skora et al. \(2015\)](#), phase proportions cannot be corrected for exsolved C-O-H volatiles. The mass balance for epidotes in run BS_c3 (800°C) was adjusted slightly on the basis of visual estimates, as noted in Table 2. Major element compositions of minerals are given in SD Table 1. Glass compositions are reported in Tables 3 (BS major elements), 4 (AS major elements), 5 (trace elements) and in SD Table 2 (additional SIMS data).

Representative SEM images of run products are given in Figures 4a-d (BS) and 5a-d (AS). They show that experiments produce relatively coarse-grained (approximately >20 µm sized) carbonate crystals, alongside silicates, including clinopyroxene, garnet, kyanite, SiO₂, epidote Fe-sulfides and accessory phases that are all mostly fine-grained (approximately 2-20 µm). Similar assemblages also occur in UHP terrains, e.g. in impure marbles found in Sulu, China ([Proyer et al., 2014](#); see [Skora et al., 2015](#) for more examples of epidote in UHP terrains). Fe-sulfides are also ubiquitous in formerly subducted rocks, although we note that in nature, sulfides are chemically more complex due to the presence of Cu, Ni etc (e.g. [Liu et al., 2009](#); [Evans et al., 2014](#); [Tomkins and Evans, 2015](#)).

All experiments produced abundant microvesicular glass suggesting that significant proportions of volatiles exsolved upon quench. The ubiquity of glass constrains the water-present solidus to be below 800°C, in concordance with [Skora et al. \(2015\)](#). The melting reaction is not determined in this experimental sequence, but the observed residual phases are

consistent with previous experimental melting studies of carbon-bearing sediments in the presence of excess water (e.g. [Thomsen and Schmidt 2008a, 2008b](#), [Tsuno and Dasgupta, 2012](#); [Skora et al., 2015](#)). All runs show evidence of a second fluid phase that co-exists with volatile-rich melts, in agreement with previous experiments on similar compositions (e.g. [Thomsen and Schmidt 2008a](#), [Skora et al., 2015](#)). Graphite was not observed in any run product.

A noteworthy difference in phase petrology is documented between BS and sulfur-free AS1 and AS2 run products, and AS1+FeS₂ and AS2+FeS₂ run products (Table 2). The former are marked by the presence of clinopyroxene ± epidote ± Fe³⁺-rich oxide, whereas in the latter the only residual phase beside carbonate and sulfide is garnet. We attribute this difference to varying *f*O₂ conditions that are imposed by the various starting materials (see section 4.1).

3.2 Mineral chemistry

Ferric iron contents are computed by the method of [Droop \(1987\)](#) for garnet and clinopyroxene. For other minerals, e.g. epidote, stoichiometric considerations are used. *Clinopyroxenes* occur in all BS and in certain AS1 and AS2 run products. They classify as Ca-Na pyroxenes, containing a significant Fe-Mg-Ca component (approximately 50–60%). The calculated aegirine component varies from approximately 13–22 mol% in BS and AS1 run products without additional FeS, to 5–9% in BS+FeS and 2–6% in AS2 run products. A mineral phase of the *epidote-clinozoisite* solid solution occurs in some runs (Table 2). The epidote component is particularly dominant in the BS and AS1 run products (>80%), in contrast to AS2 run products (approximately 50% epidote-component). The presence of *garnet* is restricted to AS1+FeS₂ and AS2+FeS₂ run products; it occurs in trace amounts in a single BS+FeS run (BS_c5). Garnet composition is strongly bulk rock-dependent: in the BS runs it is rich in almandine (~44%), grossular (~36%), pyrope (~9%) and andradite (~10%); in AS1_FeS₂ runs it comprises grossular (~46%), almandine (~35%), pyrope (~12%), andradite (~6%) and spessartine (~1%); in AS2_FeS₂ runs garnet is composed of almandine (~52–

53%), grossular (~21–25%), pyrope (~19–20 %), andradite (~0–6%) and spessartine (2%). Residual carbonate is almost pure calcite with an $X_{Ca} \geq 0.95$ ($X_{Ca}=Ca/[Ca+Mg+Fe]$). In two runs with the BS+FeS composition, carbonates contain a higher Fe-Mg component ($X_{Ca} \geq 0.89–0.93$). Other trace or accessory phases found in some runs include apatite, crystalline SiO₂, titanite, kyanite and Fe³⁺-rich Fe-Ti-oxide. Rutile is also present in TiO₂-doped AS2 runs.

Residual sulfide is identified as either pyrrhotite (Fe(1-x)S; x=0–0.17) or pyrite (FeS₂), regardless of the source of sulfur in the starting material (Table 2; SD Table 1). For example, pyrrhotite reacted to form pyrite in BS_c5, whereas it remained as pyrrhotite in all other runs (starting material = BS+FeS). In contrast, pyrite reacted to form pyrrhotite in run AS2_e6 and AS1_e5 whereas it remained pyrite in run AS2_e8 (starting materials = AS1 & AS2+FeS₂). It is beyond the scope of this study to narrow down the issue of sulfide stability at sub-arc conditions, but an extended discussion can be found in [Tomkins and Evans \(2015\)](#). For our purposes, it is only of importance to show that both types of sulfide can host significant Mo, as suggested by significantly reduced Mo concentrations in glasses in the presence of sulfide. In addition, Mo concentrations in glasses are approximately constant irrespective of the residual sulfide phase (Table 5). This implies that Mo has at least approached equilibrium, even in experiments where the identified sulfide phase was the original source of sulfur.

3.3 Melt chemistry

Experimental glasses are rich in SiO₂, Al₂O₃, CaO, K₂O and Na₂O, and can be classified as peraluminous to metaluminous granites. The ASI index (molar Al/[Ca-1.67P+Na+K]) varies from 0.8–1.3 in both starting materials (Tables 3 and 4). Figure 6a-d and 7a-f illustrate the systematic changes of selected major and trace elements, respectively, of glass over the small temperature interval investigated (800–900°C, BS only). For example, SiO₂ and K₂O mainly follow a dilution trend in the absence of significant amounts of quartz/coesite and phengite (Fig. 6a-b, Table 2). In contrast, CaO concentrations increase

steadily with temperature as increasing amounts of clinopyroxene, epidote and carbonate dissolve in the melt (Fig. 6c, Table 2). Similar trends are evident for MgO, FeO and TiO₂, likely reflecting progressive dissolution of mainly clinopyroxene and titanite (Table 3). In contrast, Al₂O₃ and Na₂O vary little in their concentrations. The ASI decreases below 1 with increasing temperature (Fig. 6d).

Mass balance calculations for trace elements are presented in SD Table 3, along with the proportion of the original trace element budget contained in the melt phase (in %). This is the proportion of an element that has the potential to be recycled via magmatism to the Earth's surface (termed "recycling efficiencies"). These are not straightforward calculations. For example, an unknown quantity of C-O-H fluids exsolves upon quenching as evidenced by highly microvesicular glasses (see also [Skora et al., 2015](#)), leading to a passive enrichment of trace and major elements in quenched glasses. As a consequence, mass balances of perfectly incompatible elements lead to recycling efficiencies in excess of 100%. We therefore work with "apparent" melt fractions, which are calculated assuming that Cs, the most incompatible element, in the absence of phengite (e.g. [Melzer and Wunder, 2000](#); [Hermann and Rubatto, 2009](#)), is quantitatively incorporated into the melt phase. The recycling efficiencies of all other trace elements are thus given relative to the mobility of Cs (with assumed 100% recycling efficiency).

Trace element patterns in glasses are strongly tied to the residual mineralogy. Elements without a solid host, such as Rb (and Cs), are fully incompatible and follow a dilution trend (Fig. 7a, SD Table 3). In contrast, Sr concentrations in glasses steadily increase with increasing temperature. This likely reflects a temperature-dependent change in the K_D of Sr between Ca-rich minerals such as carbonate, apatite, clinopyroxene and melt (Fig. 7b), as well as progressive dissolution of its host minerals. Elements such as Nb and Ta are almost perfectly incompatible in all experiments that lack residual rutile (SD Table 3). Heavy REE+Y concentrations in glasses are very low in all garnet-bearing experiments (Table 5),

but significant fractions of these elements are also hosted by carbonate (SD Table 4, Skora et al., 2015)

It is well known that LREE(+Th) can be hosted by carbonate (Skora et al., 2015) as well as by accessory phases such as epidote-group minerals, monazite and apatite (e.g. Hermann, 2002; Klimm et al., 2008; Hermann and Rubatto, 2009; Carter et al., 2015). Apatite is readily identified in all BS run products; its presence is linked to the high bulk P_2O_5 content of black shales. Epidote is an important host for LREE(+Th) in some BS experiments, as well as in all AS1 and AS2 experiments that experienced oxidised conditions (Table 2). Light REE(+Th) concentrations in glasses are particularly low in these runs (Fig. 7c-d), with e.g. less than 5% of bulk LREE being contained in the melt phase. In contrast, approximately 20–60% of the original LREE budget is located in the melt phase (SD Table 3) from epidote-free runs, with the remainder being included in apatite and/or carbonate. Lastly, it is apparent that Mo behaves mostly incompatibly in the absence of residual sulfides, such that ~70–90% of the bulk Mo is contained in melt phase (Figs. 7e and 8, SD Table 3). In contrast, experiments that contain residual sulfides suggest that only 20–40% of bulk Mo is contained in melt (Figs. 7e and 8). Possible host phases for molybdenum besides sulfides are discussed in section 4.2. All BS, AS1, AS2, BS_FeS and AS1_FeS2 experimental run products exhibit $Ce/Mo^{melt} < 1$ (0.05–0.56), despite their differences in phase petrology (Fig. 7f, Table 2). Only AS2_FeS2 run products exhibit slightly higher Ce/Mo on the order of 2–5 (Table 5). Note in this context that BS and AS1 starting materials reflect natural Ce/Mo ($Ce/Mo^{bulk} = 0.39-0.95$ similar to $Ce/Mo^{bulk \text{ in nature}} \approx 0.3$ see section 4.4), whereas AS2 is doped in Mo ($Ce/Mo^{bulk} = 2.84$ instead of $Ce/Mo^{bulk \text{ in nature}} \approx >50$, see section 4.4). Those results will be extrapolated to natural concentrations in the discussion section.

3.4 Ce and Mo concentrations of other relevant partial melting studies

We further analysed Mo in previously published run products of relevant partial melting experiments. The runs vc4 (850°C) and vc9 (900°C), using natural volcanoclastics

438 from the Mariana arc (Martindale et al., 2013), contain the assemblage: garnet +
439 orthopyroxene + glass + Fe-Ti oxides + rutile $\pm$ clinopyroxene $\pm$ biotite $\pm$ SiO₂-phase, and
440 apatite is assumed to be present based on mass balance considerations. The bulk Ce
441 concentration is 42 ± 1 $\mu\text{g/g}$ (Martindale et al., 2013); the bulk Mo concentration of this
442 sample is unknown but the study of Freymuth et al. (2015) suggests that it should be on the
443 order of 0.4 ± 0.1 $\mu\text{g/g}$. Thus, the Ce/Mo of bulk volcanics is around 105. Cerium is
444 enriched in experimentally produced partial melts (52 ± 4 $\mu\text{g/g}$ in vc4 and 43 ± 7 $\mu\text{g/g}$ in vc9),
445 which represents approximately 70% of the bulk Ce. The remaining Ce is likely retained by
446 trace apatite (Martindale et al., 2013). New SIMS analyses of Mo concentrations revealed low
447 concentrations with 0.34 ± 0.05 $\mu\text{g/g}$ and 0.48 ± 0.09 $\mu\text{g/g}$, respectively. This implies that 50–
448 80% of the bulk Mo originally bound in volcanics is mobilized during partial melting.
449 The measured Ce/Mo^{melt} are consequently high: 153 and 90 in vc4 and vc9, respectively.

450 The runs LCA0 rep (750°C), LCA2B (800°C), LCA1 (850°C) and LCA3 (900°C),
451 used a natural sample of altered, basaltic oceanic crust (AOC) from the Mid-Atlantic Ridge as
452 starting material and contain the assemblage: garnet + clinopyroxene + glass + rutile +
453 epidote $\pm$ Fe-Ti oxides $\pm$ kyanite (Carter et al., 2015). The bulk Ce concentration is 13 ± 1
454 $\mu\text{g/g}$ (Carter et al., 2013); new analyses of the bulk Mo of the starting material is quantified at
455 1.5 ± 0.6 $\mu\text{g/g}$, which is in line with Mo concentrations in Pacific AOC (Freymuth et al.,
456 2015). Thus, the Ce/Mo of bulk AOC is around 9. The Ce concentrations in the melts are
457 quantified at 0.08 ± 0.02 $\mu\text{g/g}$, 1.1 ± 0.1 $\mu\text{g/g}$, 0.09 ± 0.01 $\mu\text{g/g}$ and 0.9 ± 0.1 $\mu\text{g/g}$,
458 respectively (Carter et al., 2015). This suggests that only about 0.1–3% of bulk Ce is
459 mobilized from basalt during partial melting in the presence of residual epidote. In contrast,
460 new analyses of Mo concentrations are quantified at 3.1 ± 0.8 ppm, 0.7 ± 0.1 ppm, 1.9 ± 0.2
461 ppm, and 4.5 ± 0.3 ppm. Thus, less than 50% of bulk Mo is released in partial melts at 750–
462 850°C, but this exceeds 50% at higher temperatures ($\geq 900^\circ\text{C}$). The Ce/Mo ratios of the AOC
463 melts are well below 1 (Ce/Mo^{melt} = 0.02–0.2) with one exception, run LCA2B (Ce/Mo^{melt} =

1.6). Note that as both studies used natural rock powder without any additional doping, Ce/Mo^{melt} are directly comparable to nature.

4. DISCUSSION

4.1 Phase petrology and redox conditions

The influence of varying fO_2 conditions and bulk Fe³⁺/Fe^{tot} on phase petrology in slab lithologies at sub-arc depth has received little attention, probably because it is inherently difficult to buffer redox conditions in piston cylinder experiments. Nor is it easy to obtain precise *in-situ* Fe²⁺/Fe³⁺ data on minerals and glasses. Fortunately, there is some qualitative information on Fe²⁺/Fe³⁺ variability in our dataset as deduced from calculated ferric iron mineral contents, using EMPA data. Although it is well known that such calculated ferric iron components are not always accurate and rather variable (e.g. [Ravna and Paquin, 2004](#); [Proyer et al., 2004](#)), they show systematic trends, which can be correlated to expected oxidation states as imposed by the various starting materials.

The largest calculated ferric iron components (e.g. epidote) occur in BS and AS1 run products that did not contain any initial sulfides (see section 3.2). The AS1 runs also contain a significant amount of Fe³⁺-rich Fe-Ti oxides. Both bulk rock compositions are very carbonate-rich (Table 1), and BS1 further contains a small quantity of sulfate. These are considered the most oxidised run products. The aegirine and epidote component is lower in all AS2 run products, but Fe³⁺-rich Fe-Ti oxides are abundant, again suggesting relatively oxidised conditions. In contrast, the aegirine component is significantly lower in all BS_FeS, compared to BS run products, and one run even contained some small quantities of garnet (BS_c5). It is a marked feature of all AS1_FeS2 and AS2_FeS2 run products that they exhibit garnet instead of clinopyroxene ± epidote ± Fe-Ti oxide. A small andradite component can be calculated for these garnets, but other Fe³⁺-bearing phases are absent. These experiments have by far the smallest estimated bulk Fe³⁺ content. Relative redox conditions of our experimental

run products are thus inferred to be as follows: BS, AS1, AS2 are oxidised; BS_FeS experimental run products are moderately oxidised; AS1_FeS2 and AS2_FeS2 are reduced.

In combination, the observations suggest that the addition of sulfates to the starting materials always leads to oxidised conditions. Solid sulfides are not found in BS experimental run products, and must consequently have become dissolved in the melt. Additional sulfides in the BS starting material, in turn, lead to slightly more reduced conditions (BS_FeS runs). Surprisingly there are abundant signs of oxidised conditions in all AS1 and AS2 runs that neither contained initial sulfate nor sulfide. This implies that oxidation via H₂ exchange is significant in such volatile-rich experiments. Initial sulfides in AS1_FeS2 and AS2_FeS2 led to the most reduced experimental run products of this study.

We can further investigate possible redox reactions amongst the silicates. For example, it is apparent from Table 2 that under oxidised conditions clinopyroxene, kyanite, epidote (solid solution) and Fe³⁺-rich Fe-Ti oxides prevail over garnets, which are restricted to relatively reduced experiments. We can write a possible reaction in the system CaO-FeO-MgO-Al₂O₃-SiO₂-H₂O-O of the form:

that is consistent with the observed phase changes. A variant of this reaction:

could explain the absence of oxides in BS run products. Although these reactions are not unique, they suggest that the presence of garnet is restricted to more reduced conditions, whereas epidote is present at oxidised conditions. This is consistent with qualitative observations provided in [Skora et al. \(2015\)](#). Such reactions are likely restricted to carbonate-rich sediments (and possibly mid-ocean ridge basalt, MORB), given that typical sediments lack sufficient CaO to stabilize epidote-group minerals.

4.2 Hosts for Mo (and Ce) during melting of subducted slabs

Light REEs are well known to have a variety of possible hosts in subducted lithologies at near-solidus conditions, namely epidote-group minerals, monazite, apatite and carbonate (e.g. [Hermann, 2002](#); [Klimm et al., 2008](#); [Hermann and Rubatto, 2009](#); this study). Sulfides are known to host significant Mo, and there is an intimate relationship between sulfides and Mo enrichments e.g. in deep-sea sediments (e.g. [Helz et al., 1996](#)) and porphyry copper-molybdenum-gold deposits (e.g. [Sillitoe, 2010](#); [Wilkinson 2013](#)). It is likely that sulfides remain a host for Mo in subducted crust, given that trace pyrite and other sulfides are reported to be stable in blueschist to UHP eclogites worldwide (e.g. [Liu et al., 2009](#); [Evans et al., 2014](#); [Tomkins and Evans, 2015](#)), as well as in relevant experimental studies (e.g. [Jego and Dasgupta, 2013](#)). However, partitioning studies between monosulfide solid solutions (MSS: Ni-Cu-bearing sulfur phase thought to crystallize at mantle conditions) and basaltic melts at mantle conditions imply that Mo is only moderately compatible in MSS, but its preference for sulfides is enhanced at reduced conditions (e.g. [Li and Audetat, 2012](#); [Li, 2014](#)). Unfortunately, residual sulfides in our study were too small to be reliably analysed for Mo, but their role as residual solid host is readily demonstrated by the reduced Mo concentrations in sulfide-saturated melts. Our experiments also confirm qualitatively that Mo is only moderately compatible in sulfides, given that 20–40% of the bulk Mo still remains in the melt phase even in experimental run products containing significant residual FeS or FeS₂ (Figs. 4a-d and 5a-d). Besides sulfides, little is known about other possible hosts of Mo in eclogites. [Zack et al. \(2002\)](#) demonstrated that some small quantities of Mo could, in principle, be incorporated into all eclogitic minerals (e.g. garnet, clinopyroxene), with rutile being by far the most effective host when considering its low abundance. We also find that a small fraction of Mo can be contained in residual silicates such as clinopyroxene; only 70–90% of bulk Mo is contained in the melt in rutile- and sulfide-free experiments. [Bali et al. \(2012\)](#) have also noted that Mo is compatible in rutile, but only at reducing conditions. This is related to the fact that Mo⁴⁺ is strongly compatible in rutile due to its favorable valence and ionic radius.

This is illustrated in Figure 9, where the position of the Mo^{4+} ionic radius is superimposed on the fitted lattice strain parabola of Klemme et al. (2005). In fact, Mo^{4+} sits right on the apex of the parabola, and should therefore be more compatible in rutile than Zr^{4+} or Hf^{4+} . As the transition of Mo^{4+} to Mo^{6+} is melt chemistry-sensitive and should spread over approximately 4 log units in $f\text{O}_2$ space, the bulk Mo partition coefficient $K_{\text{D Mo bulk}^{\text{rt-melt}}} = [\text{Mo}^{4+} + \text{Mo}^{6+}]_{\text{rt}} / [\text{Mo}^{4+} + \text{Mo}^{6+}]_{\text{melt}}$ should vary significantly over geologically relevant $f\text{O}_2$'s (e.g. Bali et al., 2012).

We have attempted to quantify Mo in rutile using EMPA (see Methods section). Average rutile Mo concentrations in run AS2_e7 (oxidised experiment without FeS) are below the detection limit ($\sim 40 \mu\text{g/g}$). Furthermore, mass balances (SD Table 3) suggest that most of the Mo is contained in the melt phase, suggesting that Mo is mostly present as Mo^{6+} and therefore not compatible in rutile. In contrast, higher Mo concentrations on the order of $70 \pm 20 \mu\text{g/g}$ ($n=16$) are suggested for rutile in run AS2_e8 (reduced experiment with FeS), corresponding to $K_{\text{D Mo bulk}^{\text{rt-melt}}} \approx 4$. These results confirm the redox-sensitive role of rutile in hosting Mo.

Lastly, we note the presence of other accessory phases such as titanite and Fe^{3+} -rich Fe-Ti-oxide in our experimental run products and in nature. Unfortunately, these phases were too small to be quantified but Ce, for example, is known to be moderately compatible in titanite (e.g. Prowatke and Klemme 2005). By analogy with 4+-ions substituting for Ti in rutile, it is reasonable to expect that some Mo can be hosted by titanite at sufficiently reduced conditions. The Fe^{3+} -rich Fe-Ti-oxides, in contrast, are unlikely to contain significant Mo or Ce, due to the predominance of hematite in the solid solution and the size-charge mismatch between Mo^{4+} and Fe^{3+} .

4.3 Behaviour of Mo and Ce during melting of black shales (BS & AS1) and average calcareous sediment (AS2)

Our experimental sequence suggests that variations in redox conditions control Ce/Mo ratios of partial melts generated from calcareous black shales (BS & AS1). The Ce/Mo ratio of these starting materials is low (0.39 and 0.95 respectively), which is close to natural Ce/Mo ratios in the anoxic layer in DSDP leg 14 Site 144 (0.27–0.30: [Carpentier et al., 2009](#) and [Freymuth et al., 2016](#)). The lowest measured Ce/Mo ratios in experimental glasses ($\ll 1$) are restricted to carbonate-bearing and sulfide-absent (oxidised) run products (Tables 2, 5). The Ce/Mo ratios are particularly low when epidote is present because both epidote and carbonate scavenge significant quantities of Ce. Molybdenum, in contrast, is mostly incompatible in these runs in the absence of a preferred host (Fig. 8a-b).

Experimental run products with carbonate $\pm$ trace epidote and additional sulfides (i.e. more reduced experiments) exhibit slightly higher Ce/Mo in glass as some quantity of Mo is sequestered from the melt into sulfides. Note that measured Ce/Mo still remain <0.1 , despite the fact that relative mobilities (or recycling efficiencies) of Mo and Ce are comparable in these experiments (SD Table 3). This is due to generally low Ce concentrations in carbonate-rich sediments, in contrast to Mo that is enriched in black shales (bulk Ce/Mo ~ 0.3).

In other calcareous sediments (AS2), measured Ce/Mo ratios in melts are again <1 in oxidised experiments due to the presence of residual epidote. Conversely, $\text{Ce/Mo}^{\text{melt}}$ is >1 in all AS2_FeS experiments that record reducing conditions because these run products are free of epidote, but rich in sulfides $\pm$ rutile. Unfortunately, we cannot deconvolve the effects of sulfide versus rutile given that we lack experimental run products at reducing conditions that contain only rutile. That Ce/Mo ratios in glass remain low ($\sim 2\text{--}5$) is because the bulk Mo concentration in AS2 is not representative of average calcareous sediments (Mo $\sim 31 \mu\text{g/g}$ instead of $\sim 1 \mu\text{g/g}$ in average marine sediments, e.g. [Freymuth et al., 2015](#)), suggesting that natural $\text{Ce/Mo}^{\text{melt}}$ be much higher at equivalent reducing conditions, possibly on the order of 160–210.

We conclude that melting of carbonaceous black shales in an oxidising environment is likely to lead to Ce/Mo in partial melts that are $\ll 1$ given that residual epidote and carbonate will lead to particularly low LREE concentrations. In addition, sulfides are destabilized and Mo^{6+} appears incompatible in rutile. Thus, Mo has no major host and behaves incompatibly (Fig. 8a-b). The Ce/Mo ratio is higher at more reduced conditions, but likely remains < 1 in partial melts of black shales, due to significantly lower Mo concentrations in sulfide-saturated melts, the greater compatibility of Mo^{4+} in rutile, and low bulk Ce/Mo < 1 . Oxidising conditions are thus much more favorable for the transfer of Mo from a black shale lithology into the mantle wedge (Fig. 8a-b). Extending these observations to nature is compromised by our limited knowledge of prevailing redox conditions of the various slab lithologies, and the dependence of $\text{Mo}^{4+}/\text{Mo}^{6+}$ ratios in melts and fluids on redox state. For example, it is not known whether oxygen-deficient black shales would undergo melting in an oxidising environment during subduction due to the presence of oxidised lithologies elsewhere in the subducting slab, or whether graphite-bearing black shales would impose their own local reduced environment. Still, given that black shales are by far the most dominant supplier of Mo in the subducted column, even if only 20% of bulk Mo is transferred to the mantle wedge it will have a significant influence of the total Mo elemental and isotopic budget. Most important however is the fact that arc lavas with a distinct, isotopically heavy Mo isotopic signature of black shales are characterized by Ce/Mo $\gg 1$ (Fig. 2b), whereas all partial melts of calcareous black shale compositions exhibit Ce/Mo < 1 . In the following section, we therefore explore the possibility of a decoupled transfer of LREE and Mo of different subducted layers.

4.4 Behaviour of Mo and Ce during melting of other sediment types (Lesser Antilles)

There are a number of published partial melting studies that use synthetic or natural sediments: radiolarian clay (Skora and Bundy, 2010); terrigenous sediment (Skora and

Bundy, 2012); calcareous clay (Thomsen and Schmidt, 2008a; Skora et al., 2015; AS2 composition of this study) and carbonate-rich marls (Skora et al., 2015). The melting phase relations of a GLOSS-like composition (Plank and Langmuir, 1998) are provided by Hermann and Spandler (2008) and Hermann and Rubatto (2009). After accounting for the effects of variable doping levels we can use these data to infer the behavior of Mo and Ce in the subducted slab beneath the Lesser Antilles arc, where representatives of all of these lithologies are likely to occur.

Terrigenous sediments, radiolarian clay and *GLOSS* are relatively CaO-poor and bulk LREE concentrations are typically high (bulk LREE ~ 100–200 µg/g, bulk Ce ~ 50–100 µg/g: Carpentier et al., 2009). Average bulk Mo ratios of such terrigenous sediments and clays are unknown, but assuming that a typical Mo concentration in marine sediments is around 1 µg/g (Freymuth et al., 2015), it is suggested that Ce/Mo^{bulk} is on the order of 50–100, with the potential to vary widely. The most likely host for Ce in CaO-poor but P₂O₅-bearing sediment is monazite. The influence of P–T and redox state on the presence of allanite/epidote versus monazite in CaO poor sediments is not well studied, but monazite was always the sole residual LREE host in the experiments of Skora et al. (2010) and (2012), even at relatively oxidised conditions. High total LREE concentrations on the order of 100–250 µg/g (Ce ~ 50–125 µg/g) are suggested to be present in near-solidus partial melts in the presence of monazite (e.g. Hermann and Rubatto, 2009; Skora and Blundy, 2012). Assuming that bulk Mo is perfectly incompatible at oxidising conditions, ~2–5 µg/g Mo could be contained in sediment-derived partial melts assuming a melt fraction (F) of 0.2–0.5. However, at reduced conditions in the presence of trace sulfides and rutile, a certain quantity of Mo will be retained. If only 20% is mobilized Mo concentrations in melts could be reduced to ~0.4–2 µg/g. Thus Ce/Mo of partial melts of terrigenous sediment and marine clay could vary widely, being on the order of 10–300.

Calcareous clay and marls are variably rich in CaO (Fig. 3), and bulk LREE concentrations are lower than in marine clay (bulk LREE ~ 20–130 µg/g, bulk Ce ~ 10–60 µg/g; [Carpentier et al., 2009](#)). The data of [Carpentier et al. \(2009\)](#) further suggest that the calcareous material mainly serves to dilute the trace element signal, suggesting that Ce/Mo of calcareous clays and marls is little different to that of other marine sediments. Indeed, data of [Carpentier et al. \(2009\)](#) in combination with [Freymuth et al. \(2016\)](#) reveal that Ce/Mo^{bulk} from DSDP leg 14 Site 144 is ~120–246 for 3 oxic calcareous sediments. At sub-arc conditions, it appears that an epidote-group mineral is often stable in these compositions (e.g. [Skora et al., 2015](#); this study), although its exact stability field is a complex function of bulk rock chemistry and redox conditions (e.g. [Holdaway, 1972](#); [Liou 1973](#); [Liou et al., 1983](#); [Poli and Schmidt, 2004](#)). Run products using the AS2_FeS composition appear to be sufficiently CaO-poor and reduced that epidote is no longer present above 850°C, 3 GPa. Carbonate can also host significant quantities of REE ([Skora et al., 2015](#); this study). Light REE concentrations in near-solidus melts are only ~5–10 µg/g (Ce ~ 2–5 µg/g) in the presence of residual carbonate and epidote (e.g. [Skora et al., 2015](#); this study). The same considerations for Mo as described above apply for calcareous clay and marls. Thus the Ce/Mo of partial melts of calcareous lithologies are likely to be low, on the order of 0.4–13. Only relatively CaO-poor compositions have the possibility to carry a Ce/Mo signal that is significantly larger, if melting occurs at conditions sufficiently reduced to eliminate epidote from the residue. For example, AS experimental run products, extrapolated to natural Ce/Mo concentrations should have Ce/Mo ratios of 160–210 in near-solidus partial melts.

We conclude that terrigenous sediment and other CaO-poor marine clays will be the most potent contributor of Ce and other LREE, due to their high bulk LREE and melting in the presence of monazite. In contrast, relatively little LREE can be extracted from carbonate-rich clays and marls, due to the presence of carbonate and epidote-group minerals. A summary is given in Figure 10, demonstrating that Ce/Mo cannot be used as a tracer of the

dominant slab component because Ce/Mo of partial melts can be very different to that of the bulk rock, because both elements are controlled by very different residual mineral phases.

4.5 Implications for the slab component in the Lesser Antilles

Lavas in the southern Lesser Antilles arc exhibit some of the most radiogenic Pb isotopic compositions found in intra-ocean island arcs worldwide. The data have been either explained by crustal contamination (e.g. [Thirlwall and Graham, 1984](#); [Davidson, 1987](#); [Smith et al., 1996](#)), variations in sediment input (e.g. [White and Dupré, 1986](#); [Turner et al., 1996](#)) or fluids/melts derived from a black shale layer ([Carpentier et al., 2008](#)). The Mo isotopic study of [Freymuth et al. \(2016\)](#) strongly supports the last suggestion (Fig. 2b). Only a fluid or melt stemming from a black shale layer rich in isotopically heavy Mo can satisfactorily explain the elevated $\delta^{98/95}\text{Mo}$ in the southern Lesser Antilles lavas. Whilst such black shales are found off-board the arc in DSDP site 144, at the edge of the Dermerara Rise, they are not believed to occur on the over-riding plate on which the volcanic edifices are built. Thus, the distinctive Mo isotopic signature must come from subduction not contamination [Freymuth et al. \(2016\)](#).

Figure 2b further suggests that the fluid/melt component with elevated $\delta^{98/95}\text{Mo}$ is characterized by a high Ce/Mo ratio, exceeding 50. One of the main conclusions of the experimental study is that partial melts of a carbon-rich black shale layer such as drilled in DSDP leg 14 Site 144 would be rich in Mo, but their Ce/Mo would be very low (<1). It is therefore suggested that Ce is mostly derived from marine clay and terrigenous sediment. Sediments drilled at the edge of the Dermerara Rise however lack marine clays and terrigenous sediment altogether. The other calcareous units of DSDP leg 14 Site 144, cannot satisfactorily explain the enrichment of Ce over Mo, because epidote and carbonate would retain most of the bulk Ce during partial melting. This implies that sediments of that drill site cannot be taken as a proxy for sediment subduction in the Lesser Antilles. The geological situation of the Dermerara Rise, a submarine plateau lying in relatively shallow waters (~ 700 m) and favouring accumulation of calcareous sediments, may be unusual indeed. Most

sediments that are of comparable ages in DSDP leg 78 Site 543 (off the coast of Dominica), are CaO-poor marine clays and terrigenous sediments (Fig. 1a, [Plank and Langmuir, 1998](#); [Carpentier et al., 2009](#)). The only exception is a small layer of sediments (75–65 Ma) that is directly overlying the igneous mafic crust, which is described as calcareous clay. Black shales in DSDP leg 14 Site 144 are even older than this unit, being 102–80 Ma in age (Fig. 1a). Records of the Oceanic Anoxic Event at ~96–93 Ma event can be found through large parts of the Atlantic oceanic basin, even in deep-sea sediments (e.g. [Arthur, 1979](#)). It is therefore well conceivable that the paleogeological situation allowed for the ubiquitous deposition of anoxic layers off the coast of the Lesser Antilles. Thus, we conclude that although the bulk sediments drilled in DSDP leg 14 Site 144 might not be representative for formerly subducted sediments, an anoxic sediment component was very likely present on the subducting Atlantic sea-floor in the geological past, confirming the suggestion of [Carpentier et al. \(2008\)](#).

4.6 Behaviour of Mo and Ce during melting of basalt and volcanoclastics (Marianas)

[Freyer et al. \(2015\)](#) quantified $\delta^{98/95}\text{Mo}$ and Ce/Mo of mafic primitive arc lavas from the Mariana Arc, as well as its sedimentary input and variably altered MORB from the Pacific sea-floor. One of their main conclusions is that MORB-equilibrated fluids/melts have Ce/Mo < 0.1, much less than average Ce/Mo of MORB (~30, [Newsom et al., 1986](#)). This is directly confirmed by the partial melting experiments using natural basalt (AOC) of [Carter et al. \(2015\)](#): significant Ce is retained in epidote as reflected by very low Ce in partial melts (Ce ~ 0.1–1 $\mu\text{g/g}$, bulk Ce = 13 $\mu\text{g/g}$, [Carter et al., 2015](#)); whereas Mo is moderately incompatible (Mo ~ 0.7–4.5 $\mu\text{g/g}$, bulk Mo = 1.5 $\mu\text{g/g}$) (section 3.4). Measured Ce/Mo are consequently well below 1 (Ce/Mo = 0.02–0.2) with the single exception of run LCA2B (Ce/Mo = 1.6). The good agreement between natural and experimentally-derived Ce/Mo ratios of slab-derived melts highlights the importance of having sufficiently oxidised conditions in the subducted slab such that epidote is a stable residual phase, suppressing Ce/Mo in near-solids

partial melts. The one experimental run product (LCA2B, section 3.4) that is characterized by a higher Ce/Mo^{melt} (1.6) shows evidence of recording more reduced conditions than the other runs with Ce/Mo^{melt} < 1. The modal abundance of residual epidote is reduced in this run, leading to higher LREE concentrations in the melt phase. At the same time, Mo concentrations are reduced (see section 3.4). This is likely related to an enhanced proportion of Mo⁴⁺ that are compatible in rutile (Fig. 9).

We can further estimate the Ce/Mo^{melt} of more reduced conditions where epidote may not occur. The study of [Schmidt and Poli \(1998\)](#) implies, for example, that zoisite (an epidote-group mineral) is not stable above the solidus at 3 GPa. This study uses a MORB-like composition that lacks a significant ferric iron component. Light REE in near-solidus partial melts would be relatively high in the absence of a solid host. Alternatively, residual allanite could potentially be stable (e.g. [Hermann, 2002](#); [Klimm et al., 2008](#)), limiting LREE(=ΣLa-Sm) to approx. 40-75 ppm in partial melts at 800-850°C. Extrapolating the data of [Klimm et al. \(2008\)](#) to natural LREE abundances, Ce concentrations are calculated to be around 15–30 µg/g in allanite-saturated melts at 800-850°C. When combined with Mo concentrations given in section 3.4 (750–850°C), Ce/Mo^{melt} would be relatively high, on the order of 5–40, which is inconsistent with the observation of [Freymuth et al. \(2015\)](#). This supports the idea that melting of the basaltic crust beneath the Marianas occurs at relatively oxidised conditions in the presence of epidote. We thus suggest that Ce/Mo ratios can potentially be used as a tool for roughly constraining redox conditions, through epidote stability, in any arc that is dominated by a MORB component. On the other hand, the Ce/Mo ratios of sediment-dominated arcs cannot be used for tracing redox conditions because in these Ca-poor lithologies residual allanite is supplanted by monazite, whose presence or absence is not redox sensitive.

Another inference of the Mo systematics of the Marianas presented by [Freymuth et al. \(2015\)](#) is the variable contribution of a sediment component with elevated Ce/Mo. The exact

Ce/Mo of partial melts derived from subducting sediment is not well constrained, but we suggest it is >30 . The study of [Martindale et al. \(2013\)](#) implies that LREE concentrations in partial melts derived from volcanoclastics (the most important subducting sediment type beneath the Marianas) would be relatively high, despite the fact that the bulk rock composition is too LREE-poor to saturate the melt in monazite. Molybdenum concentrations, in turn, are very low (<1 $\mu\text{g/g}$, section 3.4), due both to relatively low bulk Mo (0.4 ± 0.1 $\mu\text{g/g}$, [Freymuth et al., 2015](#)), and a relatively high bulk TiO_2 (1.8 wt%, [Martindale et al., 2013](#)), stabilising abundant residual rutile. This is reflected in the high Ce/Mo of partial melts (90–153), which readily accounts for the observations of [Freymuth et al. \(2015\)](#) (Fig. 10).

5. CONCLUSIONS

Our experimental data on element behaviour during partial melting of subducted lithologies emphasise once again the importance of particular, often accessory, residual phases in controlling key trace element ratios (e.g. [Hermann, 2002](#); [Klimm et al., 2008](#); [Hermann and Rubatto, 2009](#); [Skora and Blundy, 2010, 2012](#); [Martindale et al., 2013](#); [Carter et al., 2015](#); [Skora et al., 2015](#)). In the case of Ce/Mo the role of accessory phases is complicated by redox sensitivity of both the residual phase assemblage and the ratio of reduced and oxidised Mo species. Reduced Mo^{4+} is sequestered by residual rutile and sulphides, whereas Ce is held in epidote minerals and phosphates, whose stability (epidote only) is enhanced under oxidised conditions. Despite the complexity of Ce/Mo systematics, application of our results to two natural subduction zones (Lesser Antilles and Marianas) allow clear inferences to be drawn about the nature of the components delivered from the slab. The isotopically heavy Mo signature in the southern Lesser Antilles can be effectively delivered from subducting black shales, especially if externally buffered to more oxidised conditions. The calcareous nature of the black shales observed in DSDP site 144, however, means that Ce is retained in residual phases and the high Ce/Mo of the sediment component reflects an additional contribution from low CaO clays typically observed off-board the arc (DSDP leg

78 Site 543). In the Mariana arc, the low Ce/Mo ratio (<1) is in keeping with melts of the oxidised, altered mafic crust, which retain Ce in epidote. Ce/Mo systematics provide a valuable new means of interrogating slab melting conditions in subduction zones, especially when used in conjunction with Mo isotopes.

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Figure Captions

Figure 1a. Map of the Lesser Antilles showing the locations of the trench and the present-day active volcanic arc, as well as the positions of DSDP Legs 14 Site 144 and Leg 78 Site 543 (mbsf = metres drilled or logged below sea floor). Sediment lithologies and ages are as reported in [Carpentier et al. \(2009\)](#). Note that the age of the underlying basaltic crust increases systematically to the south, implying that older sediments can be found in DSDP leg 14 Site 144 than in DSDP Leg 78 Site 543. The Demerara Rise is a submarine plateau lying in relatively shallow waters off Surinam/French Guyana.

Figure 1b. Map of the Mariana-Izu-Bonin islands in the western Pacific showing the locations of the subduction zones, and the present-day active volcanic arc, as well as the positions of ODP Leg 129 Sites 800, 801 and 802 (mbsf = meters drilled or logged below sea floor). Sediment lithologies are as reported in [Martindale et al. \(2013\)](#).

Figure 2a. Plot of $\delta^{98/95}\text{Mo}_{\text{NIST 3134}}$ of various geochemical reservoirs after [Arnold et al. \(2004\)](#), data marked with two asterisks, and [Freymuth et al. \(2015\)](#), data marked with one asterisk. *b.* Plot of Ce/Mo versus $\delta^{98/95}\text{Mo}$ of Mariana and Lesser Antilles arc lavas (data from [Freymuth et al., 2015, 2016](#)). The isotope arrays are characterized by mixing of two reservoirs. In the Lesser Antilles, one reservoir (LA1) is low in $\delta^{98/95}\text{Mo}$ and Ce/Mo, and another reservoir (LA2) is high in $\delta^{98/95}\text{Mo}$ and Ce/Mo. The Marianas is characterized by mixing of one reservoir with high $\delta^{98/95}\text{Mo}$, but low Ce/Mo (M1), and one vice versa (M2). A reference value for depleted mantle/MORB is taken from [Freymuth et al. \(2015\)](#).

Figure 3. Chemical characteristics of sea-floor sediments off-board the Lesser Antilles, recalculated on a volatile-free basis. Sediments from DSDP Leg 14 Site 144 (black diamonds and white squares, classified using data of [Carpentier et al., 2009](#)) are mixtures of continental detritus and clay with varying proportions of carbonate. Sediments from Leg 78, site 543 are

predominantly marine clays and terrigenous sediments (striped box, representing the composition of 21 samples. Only in one unit just overlying the mafic oceanic crust (white triangles) do some calcareous sediments occur. Sedimentary starting materials BS and AS1 (grey stars) were selected to be a representative of black shales; AS2 is selected to be representative average of Antilles sediments. The melting phase relations of samples 144-16 and 144-38 are given in [Skora et al. \(2015\)](#). (Figure is adopted from [Skora et al., 2015](#); data are from [Carpentier et al., 2009](#); ESTM = experimental starting material; pl).

Figure 4a-d. (ox. = oxidised; mod. ox. = moderately oxidised experiment) Selected BSE images of experimental run products at different temperatures using the BS and BS_FeS starting materials. Partial melts are always microvesicular, due to exsolution of volatiles upon quench. Apart from carbonate and occasional epidote, residual minerals tend to be relatively fine-grained (<10 μm). Melt segregation towards the top or centre of the capsule is a common feature, which greatly aids geochemical analysis. Mineral abbreviations: cb = carbonate; ep = epidote; ap = apatite; cpx = clinopyroxene.

Figure 5a-d. (ox. = oxidised; red. = reduced experiment) Selected BSE images of AS1, AS2, AS1_FeS2 and AS2_FeS2 experimental run products at constant temperature (850°C). Run products of sulfide-free starting materials are marked by the presence of clinopyroxene $\pm$ epidote $\pm$ Fe³⁺-rich Fe-Ti oxide. Sulfide-bearing run products are petrologically distinct in that, in addition to carbonate, the only silicate residual phase is garnet. We attribute this difference to varying $f\text{O}_2$ conditions that are imposed by the various starting materials (see text). Mineral abbreviations: cb = carbonate; ep = epidote; grt = garnet; Fe-ox=iron oxides.

Figure 6a-d. Major element chemistry of quenched experimental glasses (BS run products) showing systematic changes with temperature, in accordance with changing residual phase assemblage (see text for more detail). Error bars are 1σ .

Figure 7. Trace element contents of quenched experimental glasses plotted against temperature. Trace elements are selected as representatives of different behaviours: *a.* Rb representing incompatible elements; *b.* Sr being controlled by CaO-rich minerals such as carbonate; *c.* LREE (represented by La) and *d.* Th are mainly controlled by epidote (and carbonate). *e.* Molybdenum is either enriched in the melt (white diamonds), or retained by residual sulfides where present (black squares). *f.* The Ce/Mo of melts of black shales are <1 and are particularly low in oxidised experiments (white diamonds) due to the presence of residual epidote, and the absence of a suitable host for Mo. Error bars are 1σ .

Figure 8. Plot of *a.* Mo concentration versus experimental melt fraction of BS and AS1 and *b.* Mo concentration versus experimental melt fractions of BS and AS2. The curves labeled $D(\text{Mo})=0$ denote the Mo concentrations in melts if Mo were completely incompatible in the solid residue for BS and AS1 and AS2 starting materials. Deviation of experimental melts from these curves show the extent to which Mo is retained in a suitable host mineral (sulfide $\pm$ rutile).

Figure 9. Onuma plot for trace element partition coefficients in rutile from [Klemme et al. \(2005\)](#). Superimposed is the position of the ionic radius of Mo^{4+} for a coordination number of VI suggesting that Mo^{4+} is highly compatible in rutile. This is not the case for the smaller and more highly charged Mo^{6+} .

Figure 10. Summary plot of Ce/Mo of bulk rock and associated partial melts (grey dashed line) of various geochemical reservoirs. References are: 1 = [Plank and Langmuir \(1998\)](#); 2 = [Carpentier et al. \(2009\)](#); 3 = [Martindale et al. \(2013\)](#); 4 = [Carter et al. \(2015\)](#); 5 = [Freymuth et al. \(2015\)](#); TS = this study. For simplicity, Mo is assumed to be present at a concentration of 1 $\mu\text{g/g}$ for all reservoirs for which no data were available (marine and terrigenous sediment; GLOSS; calcareous sediment). Note that MORB is likely the only lithology where Ce/Mo changes as a function of redox conditions due to the presence or absence of residual epidote as a function of $f\text{O}_2$. See the text for discussion of how Ce/Mo of the melt phase were estimated.

Table 1. Starting compositions and examples of natural subducting sediments

Majors (wt%)	ESTM's			site 144 (natural)		site 543 (natural)	
	BS	AS1	AS2	144-27*	144-1	543-21	543-4W
SiO₂	37.1	31.9	58.3	21.0	38.4	27.4	54.4
TiO₂	0.29	0.30	0.45	0.12	0.53	0.35	0.67
Al₂O₃	6.63	7.99	14.2	3.36	13.9	9.86	18.3
FeO^{tot}	2.00	4.16	7.58	1.12	5.64	5.09	7.17
MnO	0.02	0.07	0.15	0.01	0.06	0.37	0.22
MgO	1.15	1.22	2.27	0.66	1.83	1.38	1.91
CaO	26.6	28.7	6.64	28.8	14.8	25.5	0.55
Na₂O	2.83	1.52	2.79	1.83	2.24	0.89	1.71
K₂O	1.18	1.40	2.84	0.67	2.08	1.61	1.81
P₂O₅	0.69	0.18	0.30	0.46	0.14	0.18	0.15
CO₂	19.8	22.5	4.5	-	-	-	-
H₂O	0.56	-	-	-	-	-	-
SO₂	1.25	-	-	-	-	-	-
LOI	-	-	-	40.8	21.2	27.8	13.0
Sum	100	100	100	98.8	100.8	100.4	99.9
(μm/g)							
Rb	23	47	70	13.6	92.5	47.9	83.3
Sr	1100	1900	115	681	440	415	88
Y	29	18	25	13.9	18.4	31.9	24.9
Zr	-	82	114	15.5	89.4	61.4	126
Nb	-	9.2	13	1.79	11.3	7.65	13.9
Mo	58	64	31	NA	NA	NA	NA
Cs	1.9	4.0	5.7	1.12	7.25	2.96	6.92
Ba	604	1450	249	335	290	125	176
La	21	26	37	11.5	30.8	44.9	34.3
Ce	23	61	88	13.7	61.2	90.2	82.3
Nd	11	21	30	8.24	26	53.6	29.8
Sm	2.4	5.0	7.2	1.56	4.85	11.4	5.92
Lu	3.3	0.6	0.9	0.149	0.247	0.425	0.355
Hf	-	3.1	4.2	0.456	2.31	1.83	3.23
Ta	-	0.6	1.0	0.146	0.788	0.56	0.938
Th	3.5	8.6	12	2.16	10.7	9.49	12.1
U	18	6.6	4.4	13.7	1.41	0.702	1.83
Ce/Mo	0.39	0.95	2.84	ND	ND	ND	ND

Note: major and trace elements were measured on fused glass beads (in Li₂B₄O₇), volatile data are gravimetric values

LOI=loss of ignition; ESTM=experimental starting material; NA=not analyzed; ND=not defined

*sample 144-27 is a black shale; other compositions were selected to illustrate the chemical variability

Table 2. Run table and phase proportions

Run#	ESTM	T (°C)	t (h)	glass	cpx	cb	ap	ep	grt	oxides	rt	ky	minor phases
BS_c3: oxidised (*)	BS	800	120	45.0	19.0	29.0	2.0	5.0	-	-	-	-	ph?
BS_c8: oxidised	BS	850	92	50.2	19.3	28.4	2.2	trace	-	-	-	-	ttn
BS_c1: oxidised	BS	900	68	60.7	10.2	27.2	2.0	-	-	-	-	-	
BS_c5: moderately oxidised	BS_FeS	800	120	52.3	16.2	29.3	2.0	-	trace	-	-	-	ttn, SiO ₂ , py
BS_c7: moderately oxidised	BS_FeS	850	115	50.9	17.2	28.8	2.2	-	-	-	-	-	SiO ₂ , po
BS_c6: moderately oxidised	BS_FeS	900	65	59.5	8.4	29.5	2.1	-	-	-	-	-	po
AS2_e4: oxidised	AS2	850	92	61.4	22.0	trace	-	7.8		4.5	-	3.4	
AS2_e6: reduced	AS2_FeS ₂	850	70	70.8	-	1.8	-	-	25.9	-	-	-	po
AS2_e7: oxidised	AS2_TiO ₂	850	89	63.0	17.7	trace	-	8.1	-	4.7	2.0	3.0	
AS2_e8: reduced	AS2_FeS ₂ _TiO ₂	850	88	65.9	-	2.6	-	-	26.6	-	2.2	-	py
AS1_e3: oxidised	AS1	850	92	39.9	7.3	30.8	-	19.7	-	1.1	-	-	
AS1_e5: reduced	AS1_FeS ₂	850	75	49.3	-	33.1	-	-	16.9	-	-	-	po

Note: ESTM=experimental starting material

*MB (mass balance) is slightly corrected for visual estimates (in particular epidote)

Mineral abbreviations: cpx = clinopyroxene; cb = carbonate; ap = apatite; ep = epidote; grt = garnet; rt = rutile; ky = kyanite; ph = phengite; ttn = titanite; py = pyrite; po = pyrrhotite; SiO₂ = quartz or coesite

BS_Fe = BS + 2.5 wt% FeS

BS_FeS = BS + 3.8 wt% FeS

AS1_FeS₂ = AS1 + 3.8 wt% FeS₂

AS2_FeS₂ = AS2 + 3.8 wt% FeS₂

AS2_TiO₂ = AS2 + 2.3 wt% TiO₂

AS2_FeS₂_TiO₂ = AS2_FeS₂ + 2.9 wt% TiO₂

Table 3. Major and minor element composition of siliceous glasses - BS compositions

BS	BS_c3	BS_c3	BS_c8	BS_c8	BS_c1	BS_c1	BS_c3	BS_c8	BS_c1
Type	av.	1 σ	av.	1 σ	av.	1 σ	norm.	norm.	norm.
Relative Redox	ox.	ox.	ox.	ox.	ox.	ox.	ox.	ox.	ox.
T (°C)	800	800	850	850	900	900	800	850	900
N	32	32	45	45	32	32	32	45	32
(wt%)									
SiO ₂	63.5	1.3	61.9	1.2	56.7	1.8	75.0	73.1	68.8
TiO ₂	0.21	0.03	0.33	0.03	0.37	0.04	0.25	0.39	0.45
Al ₂ O ₃	11.5	0.4	11.5	0.9	10.4	0.8	13.5	13.6	12.6
FeO	0.89	0.16	1.14	0.06	2.13	0.14	1.05	1.34	2.59
MgO	0.14	0.08	0.23	0.03	0.44	0.07	0.17	0.27	0.53
CaO	2.10	0.39	3.44	0.61	6.17	1.58	2.48	4.07	7.49
Na ₂ O	3.38	0.26	3.03	0.18	3.59	0.25	3.99	3.58	4.36
K ₂ O	2.40	0.07	2.32	0.05	2.01	0.09	2.83	2.74	2.43
P ₂ O ₅	0.10	0.09	0.16	0.07	0.24	0.08	0.12	0.19	0.30
Sum	84.7	1.4	84.6	1.1	82.4	1.1	100	100	100
ASI	1.15	0.08	1.10	0.11	0.78	0.11	1.15	1.10	0.78
Mg#	0.22	0.13	0.26	0.04	0.27	0.05	0.22	0.26	0.27
BS_FeS	BS_c5	BS_c5	BS_c7	BS_c7	BS_c6	BS_c6	BS_c5	BS_c7	BS_c6
type	av.	1 σ	av.	1 σ	av.	1 σ	norm.	norm.	norm.
Relative Redox	mod. ox.	mod. ox.	mod. ox.	mod. ox.	mod. ox.	mod. ox.	mod. ox.	mod. ox.	mod. ox.
T (°C)	800	800	850	850	900	900	800	850	900
n	44	44	36	36	39	39	44	36	39
(wt%)									
SiO ₂	62.2	1.6	64.2	0.8	61.2	1.8	73.3	74.4	71.7
TiO ₂	0.27	0.04	0.31	0.03	0.38	0.03	0.32	0.36	0.45

Al₂O₃	10.8	0.3	10.6	0.2	10.5	0.4	12.7	12.3	12.3
FeO	1.19	0.24	1.76	0.10	1.65	0.10	1.41	2.03	1.94
MgO	0.22	0.04	0.26	0.03	0.31	0.03	0.26	0.30	0.36
CaO	2.90	1.00	2.82	0.72	4.60	0.70	3.42	3.26	5.39
Na₂O	3.51	0.23	3.38	0.20	4.05	0.23	4.14	3.91	4.75
K₂O	2.78	0.08	2.24	0.09	2.01	0.08	3.28	2.59	2.36
P₂O₅	0.21	0.07	0.13	0.06	0.18	0.06	0.24	0.15	0.21
Sum	84.9	1.3	86.4	0.8	85.3	1.8	100	100	100
ASI	0.96	0.09	1.02	0.08	0.82	0.06	0.96	1.02	0.82
Mg#	0.25	0.06	0.21	0.02	0.25	0.03	0.25	0.21	0.25

ASI=Al/(Ca-1.67P+Na+K); Mg#=Mg/(Mg+Fe);

uncertainty is given as 1σ of n (=number) analyses;

av=average as measured using the electron microprobe; norm.=normalized to 100

ox. = oxidized; mod. ox. = moderately oxidized

Table 4. Major and minor element composition of siliceous glasses - AS compositions

AS2	AS2_e4	AS2_e4	AS2_e6	AS2_e6	AS2_e7	AS2_e7	AS2_e4	AS2_e6	AS2_e7
type	av.	1 σ	av.	1 σ	av.	1 σ	norm.	norm.	norm.
Relative Redox	ox.	ox.	red.	red.	ox.	ox.	ox.	red.	ox.
T (°C)	850	850	850	850	850	850	850	850	850
n	28	28	27	27	23	23	28	27	23
(wt%)									
SiO₂	63.7	0.8	62.3	1.3	63.3	0.7	74.0	73.1	73.4
TiO₂	0.20	0.03	0.21	0.03	0.32	0.04	0.23	0.25	0.37
Al₂O₃	12.1	0.2	11.1	0.3	12.4	0.4	14.1	13.0	14.3
FeO	1.03	0.09	1.50	0.17	1.27	0.11	1.19	1.76	1.48
MgO	0.70	0.06	0.68	0.09	0.82	0.16	0.81	0.80	0.95
CaO	2.29	0.20	3.12	0.47	2.76	0.38	2.67	3.67	3.20
Na₂O	2.12	0.13	2.91	0.21	2.32	0.16	2.46	3.41	2.69
K₂O	3.62	0.11	3.19	0.15	2.72	0.07	4.21	3.75	3.16
P₂O₅	0.20	0.05	0.19	0.05	0.24	0.07	0.24	0.22	0.28
Sum	86.0	1.0	85.2	1.1	86.2	1.2	100	100	100
ASI	1.31	0.05	1.02	0.06	1.38	0.08	1.31	1.02	1.38
Mg#	0.55	0.06	0.45	0.07	0.53	0.12	0.55	0.45	0.53
AS2;AS1	AS2_e8	AS2_e8	AS1_e3	AS1_e3	AS1_e5	AS1_e5	AS2_e8	AS1_e3	AS1_e5
type	av.	1 σ	av.	1 σ	av.	1 σ	norm.	norm.	norm.
Relative Redox	red.	red.	ox.	ox.	red.	red.	red.	ox.	red.
T (°C)	850	850	850	850	850	850	850	850	850
n	30	30	17	17	21	21	30	17	21
(wt%)									
SiO₂	64.9	1.2	61.9	1.9	59.3	1.3	75.6	75.8	71.6
TiO₂	0.33	0.03	0.34	0.03	0.24	0.02	0.38	0.41	0.29

Al₂O₃	11.2	0.3	10.4	1.0	11.9	0.2	13.1	12.7	14.4
FeO	1.45	0.26	1.34	0.09	1.10	0.23	1.69	1.64	1.33
MgO	0.47	0.08	0.19	0.03	0.33	0.07	0.54	0.23	0.39
CaO	2.30	0.57	2.00	0.46	4.12	0.84	2.67	2.45	4.97
Na₂O	2.42	0.16	1.97	0.22	2.78	0.21	2.82	2.41	3.36
K₂O	2.54	0.09	3.43	0.29	2.81	0.13	2.96	4.20	3.39
P₂O₅	0.18	0.06	0.09	0.05	0.21	0.06	0.21	0.11	0.25
Sum	85.9	1.1	81.7	1.6	82.8	0.9	100	100	100
ASI	1.31	0.09	1.20	0.14	1.07	0.09	1.31	1.20	1.07
Mg#	0.36	0.07	0.20	0.03	0.35	0.09	0.36	0.20	0.35

ASI=Al/(Ca-1.67P+Na+K); Mg#=Mg/(Mg+Fe);

uncertainty is given as 1 σ of n (=number) analyses;

av=average as measured using the electron microprobe; norm.=normalized to 100

ox. = oxidized; red. = reduced

Table 5. Trace element composition of siliceous glasses

Run#	BS_c3	BS_c3	BS_c8	BS_c8	BS_c1	BS_c1	BS_c5	BS_c5	BS_c7	BS_c7	BS_c6	BS_c6
type	av.	1 σ	av.	1 σ	av.	1 σ	av.	1 σ	av.	1 σ	av.	1 σ
Rel. Redox	ox.	ox.	ox.	ox.	ox.	ox.	mod. ox.	mod. ox.	mod. ox.	mod. ox.	mod. ox.	mod. ox.
T (°C)	800	800	850	850	900	900	800	800	850	850	900	900
n	2	2	6	6	6	6	8	8	11	11	10	10
(μm)												
Rb	40	2	39	2	32	2	42	5	36	2	32	4
Sr	317	3	396	4	500	40	352	15	340	7	445	3
Y	1.8	0.1	7.0	0.4	5.1	0.1	7.0	0.7	4.8	0.2	3.8	0.1
Mo	93	11	73	4	69	8	24	2	25	3	21	1
Cs	3.4	0.1	3.3	0.2	2.9	0.3	3.5	0.4	3.0	0.2	2.7	0.3
Ba	678	54	700	20	620	90	828	67	710	30	650	10
La	1.3	0.0	5.4	0.3	4.0	0.1	8.4	0.9	5.2	0.2	3.18	0.07
Ce	4.6	0.2	12.1	0.6	10.8	0.5	7.3	0.7	5.0	0.3	3.28	0.09
Nd	0.60	0.03	2.1	0.2	1.79	0.09	2.4	0.3	1.8	0.1	1.44	0.03
Sm	0.17	0.00	0.47	0.05	0.40	0.03	0.48	0.08	0.39	0.07	0.31	0.02
Lu	0.25	0.02	0.99	0.06	0.72	0.03	0.79	0.10	0.65	0.04	0.54	0.01
Th	0.67	0.01	3.4	0.2	3.5	0.2	4.6	0.6	4.0	0.2	3.73	0.09
U	22	1	17.7	0.5	21	2	26	2	25	1	23.7	0.5
ΣLREE	6.6	0.2	20.1	0.7	17.0	0.6	19	1	12.4	0.4	8.2	0.1
Ce/Mo	0.049	0.006	0.17	0.01	0.16	0.02	0.31	0.04	0.20	0.02	0.153	0.009
Run#	AS2_e4	AS2_e4	AS2_e6	AS2_e6	AS2_e7	AS2_e7	AS2_e8	AS2_e8	AS1_e3	AS1_e3	AS1_e5	AS1_e5
type	av.	1 σ	av.	1 σ	av.	1 σ	av.	1 σ	av.	1 σ	av.	1 σ
Rel. Redox	ox.	ox.	red.	red.	ox.	ox.	red.	red.	ox.	ox.	red.	red.
T (°C)	850	850	850	850	850	850	850	850	850	850	850	850
n	4	4	10	10	19	19	10	10	10	10	9	9

(μm)												
Rb	94	5	87	2	88	2	84	8	100	10	81	9
Sr	91	4	90	1	110	2	78	3	570	10	1040	60
Y	6.4	0.4	0.63	0.06	7.1	0.2	1.5	0.1	1.2	0.1	1.5	0.2
Zr	127	9	86	2	125	3	79	6	120	10	110	10
Nb	18	1	14.8	0.4	1.68	0.06	1.3	0.1	18	2	14	1
Mo	23	1	13.0	0.4	26	1	17	2	71	4	20	1
Cs	8.2	0.4	7.5	0.2	9.1	0.3	11	1	8.4	0.9	7.3	0.8
Ba	310	20	250	10	302	5	280	20	2000	100	1900	200
La	0.7	0.1	26.6	0.4	0.94	0.04	17	1	0.39	0.05	5.2	0.4
Ce	5.7	0.1	62.4	0.8	2.28	0.08	40	4	4.6	0.4	11	1
Nd	0.84	0.09	15.2	0.2	0.83	0.05	11.1	0.7	0.36	0.07	2.9	0.3
Sm	0.40	0.07	1.88	0.06	0.33	0.04	1.7	0.2	0.15	0.02	0.64	0.08
Lu	0.48	0.03	0.006	0.003	0.48	0.02	0.041	0.007	0.055	0.008	0.04	0.01
Hf	4.4	0.2	3.71	0.09	4.3	0.2	3.4	0.3	4.4	0.3	4.0	0.4
Ta	1.3	0.1	1.10	0.03	0.103	0.009	0.08	0.01	1.30	0.09	1.0	0.1
Th	0.55	0.08	12.2	0.2	0.29	0.02	14	1	0.58	0.06	9.9	0.9
U	5.0	0.2	3.99	0.05	3.54	0.09	8.8	0.6	9.3	0.3	9.3	0.7
ΣLREE	7.7	0.2	106.1	0.9	4.4	0.1	70	4	5.5	0.4	20	1
Ce/Mo	0.25	0.01	4.8	0.1	0.087	0.005	2.4	0.3	0.064	0.006	0.56	0.06

uncertainty is given as 1σ of n (=number) analyses; av=average; NA=not analyzed

ox. = oxidized; mod. ox. = moderately oxidized; red. = reduced