



# Osmium isotopes in Grande Comore lavas: A new extreme among a spectrum of EM-type mantle endmembers

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## ABSTRACT

Osmium isotopes for volcanic rocks from Grande Comore, the youngest island of the Comores Archipelago, located between East Africa and Madagascar, show systematic differences between the two volcanoes of the island.  $^{187}\text{Os}/^{188}\text{Os}$  ratios (0.15–0.16) in shield-stage alkali basalts from Karthala are among the highest yet measured in ocean island basalts with >40 ppt Os. They are uniform over the whole range of Os abundances of 20–100 ppt and form nearly linear correlations with  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $^3\text{He}/^4\text{He}$  ratios. In contrast,  $^{187}\text{Os}/^{188}\text{Os}$  ratios in alkaline lavas from La Grille volcano are more variable (0.129–0.159) and negatively correlate with Os abundances, but not with Sr–Nd–He isotope ratios.

Os isotope variability of La Grille samples is consistent with shallow contamination of mantle xenolith-bearing lavas with low  $^{187}\text{Os}/^{188}\text{Os}$  lithospheric mantle and contamination of low Os magmas with high  $^{187}\text{Os}/^{188}\text{Os}$  crust. Karthala magmas are free of such shallow contamination despite the lower Os concentration in some of its lavas.

$^{187}\text{Os}/^{188}\text{Os}$  ratios (excluding contaminated samples) indicate that Grande Comore lavas represent mixtures between melts from the Comores plume and the oceanic lithospheric mantle, with La Grille mostly lithosphere-derived and Karthala plume-derived. The inferred isotopic composition of the metasomatized hydrous lithosphere is typical of the upper mantle. The high  $^{187}\text{Os}/^{188}\text{Os}$  ratio (0.159) of the Comores plume endmember requires dominance of pyroxenite (estimated to be ~60%) over peridotite in the melt source. The Comores plume forms yet another extreme among ocean island basalts in Sr–Nd–Pb–He–Os isotope space. In the global context, individual islands with enriched mantle affinities trend towards their own unique enriched mantle endmember. The global data thus do not support the existence of narrowly defined EMI and EMII components [Zindler and Hart (1986), *Chemical Geodynamics*, Ann. Rev. Earth Planet. Sci. 14, 493–571] but rather indicate that enriched components in the mantle exhibit a spectrum of mantle endmembers.

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## 1. Introduction

The Earth's mantle represents the largest geological reservoir of the Earth. It is inaccessible to direct sampling and therefore we rely on the composition of its melting products to constrain its composition and evolution. Young, mantle-derived oceanic basalts have long been known to display trace element and isotopic differences indicating that the convecting mantle shows heterogeneity that has persisted for hundreds of millions to billions of years. The compositions of these heterogeneities indicate that they were created by prior episodes of slab subduction and melt depletions. Yet important questions remain about the timing of these events, the proportions of the recycled components that were involved (e.g. continental crust, pelagic

sediment, altered oceanic crust, oceanic lithospheric mantle), the uniqueness of endmember compositions, and how they are generated.

It has been more than two decades since White (1985) and Zindler and Hart (1986) proposed that the observed range of Sr–Nd–Pb isotope ratios can be described as mixtures of depleted mantle (DMM) with a limited number of enriched “global endmember” components (HIMU, EMI, EMII). The concept that there exist a few global mantle components has since dominated the mantle geochemical literature despite increasing inconsistencies as new OIB data sets became available. For example, Barling and Goldstein (1990) found a large range in isotopic compositions in Heard Island, Indian Ocean, consistent with binary mixing between two well-constrained endmembers having compositions distinct from the Zindler and Hart (1986) mantle components. They suggested that mantle plume sources might not represent mixtures of the “global endmembers”, but instead could be composed of recycled material of unique composition and age, with the global endmembers representing

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extremes in terms of element fractionations and ages. In his review article, Hofmann (1997) used the term “isotopic flavors”, thus avoiding defined mantle component compositions but nevertheless highlighting the distinct characteristics of each “flavor”, which represent some sort of ancient and comparatively extreme chemical differentiation (Hofmann, 2003). The expanding data sets on ocean island basalts (OIB) demonstrate the variability as well as the increasingly extreme endmember compositions of the EM-flavors (e.g. Eisele et al., 2002; Elliott et al., 2007; Jackson et al., 2007). A recent compilation of global OIB data (Armienti and Gasperini, 2007) emphasizes the distinct compositions of individual ocean island isotope array endmembers that differ from the Zindler and Hart (1986) mantle components.

Here we further explore the composition of EM-type ocean island isotope arrays and their general implications for the dynamics of creation, storage and mixing of EM reservoirs. Osmium isotopes are recognized as an exceptional tracer for recycling of crust into the Earth’s mantle, due to extremely high Re/Os ratios and the resulting high Os isotope ratios in crustal rocks (Allègre and Luck, 1980; Hauri and Hart, 1993; Reisberg et al., 1993). We focus on Grande Comore Island, whose inferred plume endmember in Sr–Nd–Pb isotope space (Class et al., 1998) lies on the so-called LoNd (low  $^{143}\text{Nd}/^{144}\text{Nd}$ ) array of Hart et al. (1986), representing a hypothetical array of mixtures between the HIMU and EMI mantle components. The new data show that the Comores plume endmember is characterized by high  $^{187}\text{Os}/^{188}\text{Os}$  ratios of ~0.16, which represents a new extreme in multi-isotope space. Together with other recently discussed endmembers (Lassiter and Hauri, 1998; Elliott et al., 2007; Jackson et al., 2007) it shows that enriched components in the mantle form a spectrum of extreme compositions beyond the conventional definitions of EM mantle components (Zindler and Hart, 1986).

## 2. Geological setting and previous work

Grande Comore is the youngest island of the Comores chain in the western Indian Ocean between East Africa and Madagascar (Supplementary Fig. 1). The islands show age-progressive volcanism (Emerick and Duncan, 1982; Class et al., 1998), consistent with formation by a quasi-stationary mantle upwelling, here called the “Comores plume” (in the literature also Comore or Comoro plume). Grande Comore Island is formed by two major volcanoes, Karthala and La Grille. Karthala is an active shield volcano and La Grille is composed mainly of monogenetic cones (Bachèlery and Coudray, 1993). Grande Comore island is located on ~140 Ma-old oceanic crust of the Somali Basin (Coffin and Rabinowitz, 1987) and its lavas reflect interaction of the plume and the oceanic lithosphere (Class and Goldstein, 1997; Class et al., 1998; Claude-Ivanaj et al., 1998). Basanites from La Grille show small ranges in Sr–Nd–Pb–He isotope ratios (Späth et al., 1996; Class and Goldstein, 1997; Class et al., 2005) and reflect variable degrees of partial melting of a source containing residual amphibole, whose limited thermal stability indicates melting of the lithospheric mantle (Class and Goldstein, 1997). The compositional variability of alkali basalts from Karthala is consistent with mixing of plume- and lithosphere-derived melts. The Comores plume represents a “low  $^3\text{He}/^4\text{He}$ ” hotspot dominated by recycled  $^4\text{He}$ -rich material (Class et al., 2005).

## 3. Samples and results

The samples for Os isotope analyses were selected to cover the chemical and Sr–Nd–Pb–He isotopic range of lavas from Grande Comore (Class et al., 1998, 2005), and represent variable degrees of partial melting and fractional crystallization with MgO = 7–19 wt.% and Ni = 60–600 ppm. Os contents range from 7 to 489 ppt (Table 1; Fig. 1) and correlate positively with MgO and Ni (Fig. 2). Os concentrations reproduce well within  $\leq 15\%$  (six samples, Table 1;

Fig. 1 shows duplicate analyses with tie lines), with the exception of sample KG1 (27%). Multiple digestion of the same samples reproduced  $^{187}\text{Os}/^{188}\text{Os}$  ratios to <1.3% (six samples, Table 1) with the exception of sample G91-17A (6.5%). Re contents range from 50 to 350 ppt. Re/Os ratios negatively correlate with Os content in Karthala samples, indicating more compatible behavior of Os relative to Re during fractional crystallization.

$^{187}\text{Os}/^{188}\text{Os}$  ratios and Os contents are systematically different between the two volcanoes on Grande Comore, with only minor overlap. Shield-stage alkali basalts from Karthala have Os abundances ranging from <20 ppt to ~100 ppt (Fig. 1a). Os isotope ratios are high ( $^{187}\text{Os}/^{188}\text{Os} = 0.15\text{--}0.16$ ) relative to MORB-type mantle ( $^{187}\text{Os}/^{188}\text{Os} = 0.126$ , Gannoun et al., 2007), and are independent of Os

**Table 1**  
Re–Os abundance and Os isotope ratios of Grande Comore lavas.

	MgO (wt.%)	Ni (ppm)	Os (ppt)	Re (ppt)	$^{187}\text{Re}/^{188}\text{Os}$	$^{187}\text{Os}/^{188}\text{Os}$ $\pm 2\sigma$ *1000
<i>Karthala</i>						
K9 <sup>a</sup>	7.53	129	22.5	350	75.6	0.1580 ± 17
K10 <sup>a</sup>	9.24	169	75.8	234	14.9	0.1566 ± 6
K11 <sup>a</sup>	9.50	185	84.4	272	15.6	0.1563 ± 3
K13 <sup>a</sup>	9.30	171	46.3	260	27.2	0.1581 ± 5
			49.3	261	25.6	0.1563 ± 4
K19	10.94	256	61.4	218	17.2	0.1517 ± 3
			71.9	216	14.5	0.1498 ± 3
K26	6.11	61	6.7	265	192	0.1536 ± 30
K41	11.47	318	90.0	264	14.2	0.1515 ± 2
			100.9			0.1515 ± 2
K42	7.27	107	36.1	353	47.4	0.1542 ± 5
K44	7.04	99	13.0	261	97.4	0.1530 ± 15
<i>Old Karthala</i>						
K16	11.09	242	57.1	53	4.52	0.1406 ± 6
<i>La Grille</i>						
G16	19.06	616	176.2	193	5.28	0.1384 ± 3
			202.6	195	4.65	0.1389 ± 2
G17A	12.80	318	38.6	206	25.8	0.1383 ± 7
			33.0			0.1476 ± 7
G17B	12.97	372	45.7	181	19.1	0.1384 ± 6
			47.0			0.1370 ± 6
<i>“Contaminated”</i>						
G10	12.02	313	37.6	63	8.12	0.1585 ± 17
G12	13.04	319	32.2	270	40.6	0.1492 ± 10
KG1	12.17	305	50.3	74	7.08	0.1440 ± 5
			66.1			0.1442 ± 5
KG3	13.42	331	36.8	161	21.1	0.1497 ± 2
KG4	9.37	152	29.2	62	10.3	0.1484 ± 9
<i>“Xenocrystic”</i>						
G7	14.91	490	488.6	250	2.46	0.1288 ± 3
G7* <sup>b</sup>			89.4	250	13.5	0.1392 ± 4
G14	16.25	486	319.0	61	0.92	0.1346 ± 2
G18A	16.24	553	418.2	161	1.85	0.1345 ± 3

Osmium was extracted following the Carius tube method (Shirey and Walker, 1995), solvent extraction (Shen et al., 1996) using carbon tetrachloride and purified by subsequent micro distillation (Roy-Barman and Allègre, 1995). Re is extracted by anion exchange chromatography (Walker, 1988; Morgan and Walker, 1989). The whole procedural blank was <3 pg Os and <2 pg Re. Re and Os isotope ratios were measured at DTM, Carnegie Institution Washington following procedures as described by Pearson et al. (1995). In-run precision is given and was 0.1–1.1% (2 $\sigma$ ) for  $^{187}\text{Os}/^{188}\text{Os}$  (except K26 1.9%). Thirty-seven replicate analyses of the DTM solution standard ‘J-M Os’ run from 1995 to 2001 (and thus bracketing the production of these data in 1998) produced an average of 0.1742 ± 5 (2 $\sigma$  × 10<sup>4</sup>). This average, which was produced by pulse counting on a discrete dynode ion multiplier at low signal sizes, agrees within errors with the J-M Os standard value of 0.17399 produced with much higher signals in Faraday cups with both NTIMS and ICP-MS. MgO and Ni from Class and Goldstein (1997) and Class et al. (1998, 2005).

<sup>a</sup> Plume endmember.

<sup>b</sup> Sample G7\* was prepared by picking olivine-free chips, whereas G7 includes chips with olivines, partly probably from disaggregated xenoliths. See discussion.

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