

# 5 Oxygen Isotope Variations of Basaltic Lavas and Upper Mantle Rocks

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## INTRODUCTION

This chapter summarizes the oxygen isotope geochemistry of terrestrial basalts and their mantle sources, including the conceptual framework for interpreting such data and the phenomenology of known variations. In particular, the first section outlines the motivations for and first-order results of oxygen isotope studies of terrestrial and lunar basalts over the last 30 years; the second section reviews oxygen isotopic fractionations among phases relevant for studying basalts and mantle rocks; the third summarizes variations in  $\delta^{18}\text{O}$  of various crustal rocks that may contribute to the petrogenesis of basalts either as subducted source components or lithospheric contaminants; and the final and longest section describes observed oxygen isotope variations of major classes of terrestrial basalts and related mantle nodules with an emphasis on data generated within the last six years using laser-based fluorination techniques. In the interests of brevity, I do not describe in detail methods for oxygen isotope analysis or changes in  $\delta^{18}\text{O}$  of volcanic rocks caused by sub-solidus alteration; however, these issues are important practical considerations for anyone studying oxygen isotope compositions of basalts and interested readers are directed to the following references: analytical methods: Sharp (1990), Matthey and Macpherson (1993), and Valley et al. (1995); basalt alteration: Muehlenbachs (1986), Alt (1993), and Staudigel et al. (1995).

## GUIDING PRINCIPLES

Geochemical studies of basaltic rocks are concerned with (among other issues) identifying subducted crustal materials in their mantle sources and characterizing extent and mechanisms of their interactions with the crustal rocks they intrude. Both aims require geochemical tools capable of discriminating rocks that are now or once were part of the crust from those that have always resided in the mantle. Many crustal materials have oxygen isotope ratios that differ strongly from those characteristic of the mantle because of isotopic fractionations associated with low-temperature weathering and water-rock interaction. Therefore, oxygen is among the isotopic systems (others include H, Li, B, C, N, Cl and S) that are likely to provide measures of the role of crustal rocks in basalt petrogenesis, either as subducted source components or contaminants from the current lithosphere. This line of reasoning was perhaps put best by Taylor and Sheppard (1986), who wrote: "*We here assert the 'central dogma' of the oxygen isotope geochemistry of igneous rocks, as follows: All relatively  $^{18}\text{O}$ -rich or  $^{18}\text{O}$ -depleted silicate melts on Earth ... must have in part been derived from, or have exchanged with, a precursor material that once upon a time resided on or near the Earth's surface.*" In practical terms, 'near' the earth's surface should be defined as the portion of the lithosphere that contains hydrostatically pressured fluids; i.e. within ~10 km of the surface, where rocks undergo aqueous alteration at high water-rock ratios. The question of one's reference frame for defining  $^{18}\text{O}$ -enriched and  $^{18}\text{O}$ -depleted compositions will be considered at various points throughout this chapter.

All common rocks, melts and geological fluids span a narrow range in oxygen concentration and therefore mixing proportions of isotopically distinct components contributing to the chemistry of magmas or mantle rocks are more easily defined for oxygen than for most other isotopic systems. However, sensitivity is correspondingly poor—in general more than 1 wt % of components that are or once were from the crust must be sampled in order for a basaltic rock to differ in  $\delta^{18}\text{O}$  from a value in equilibrium with upper mantle peridotites. In this sense, oxygen isotope geochemistry differs from and potentially complements a large number of geochemical tracers involving highly incompatible elements (i.e. those elements that partition into silicate melts during melting or crystallization—such as Sr, Nd, Hf, or Pb). The principles and mathematics of mixing relationships in the combined oxygen—strontium isotope system are discussed by Taylor (1980), and Taylor and Sheppard (1986); these principles are easily extrapolated to mixing relationships involving oxygen and other elements and their mathematics will not be reviewed again here except in reference to the interpretation of particular data sets.

Finally, although the motivations for oxygen isotope studies of basaltic rocks are similar to those inspiring studies of the isotope geochemistry of several other elements, oxygen isotope variations of mantle and crustal rocks are known with greater breadth and detail than are isotopic variations of C, S and, particularly, H, Li, B, and Cl because it has been technically possible to efficiently and precisely measure the  $^{18}\text{O}/^{16}\text{O}$  ratio of most major rock types for nearly 40 years; therefore new observations can be placed in a relatively rich context.

### EARLY STUDIES OF OXYGEN ISOTOPE VARIATIONS IN MAFIC IGNEOUS ROCKS

The potential strength of oxygen isotope geochemistry to illuminate the role of crustal rocks in the petrogenesis of basalts was recognized more than 30 years ago (Taylor 1968; Anderson et al. 1971) and since this time has been explored extensively by ‘conventional’ (resistance-heated) fluorination analyses of whole rock samples. Most of these data are not reviewed in detail here both because they were recently reviewed by Harmon and Hoefs (1995), who supply an excellent data base of these measurements on request, and because geochemical records based on such measurements generally differ significantly from those produced by the more recent laser-based analyses that are emphasized in this chapter. However, it is useful to briefly review the first-order description of oxygen isotope variations of terrestrial basalts, their mantle sources, and their lunar analogues provided by these studies:

- Most terrestrial basalts and lunar rocks are similar to one another in  $^{18}\text{O}/^{16}\text{O}$  ratio and all such rocks define a common mass-dependent fractionation line in a plot of  $^{17}\text{O}/^{16}\text{O}$  vs.  $^{18}\text{O}/^{16}\text{O}$  (Clayton et al. 1972; Robert et al. 1992; Harmon and Hoefs 1995; Clayton and Mayeda 1996). These observations are generally interpreted to mean that: (1) The silicate mantles in the Earth–Moon system are made of a single, originally well-mixed oxygen reservoir; and (2) no large ( $\geq 1\%$ ) mass-dependent fractionations preferentially influenced oxygen in the lunar mantle or the terrestrial mantle during or after the formation of the Earth–Moon system (i.e. if such mass-dependent fractionations occurred they influenced the lunar and terrestrial mantles approximately equally).
- Fresh, Cenozoic oceanic basalts typically span a narrow range in  $\delta^{18}\text{O}$  (~5 to 7 ‰ for whole rocks), restricting the abundance of subducted crust in their mantle sources and crustal contaminants added to them during differentiation to amounts less than ~10 wt %. Furthermore, these data suggest that isotopic fractionations during melting, metasomatism, and metamorphism in the upper mantle are small

( $\leq 1$  ‰) on the scales sampled by erupted basalts (Harmon and Hoefs 1995).

- The weight of evidence suggests that unaltered oceanic basalts have not varied in  $\delta^{18}\text{O}$  by more than  $\sim 1$  to 2 ‰ since the mid-Archean, requiring that the integrated effects of plate tectonic evolution have not produced large shifts in the  $\delta^{18}\text{O}$  of the upper mantle (e.g. Kyser 1986; Muehlenbachs 1986).

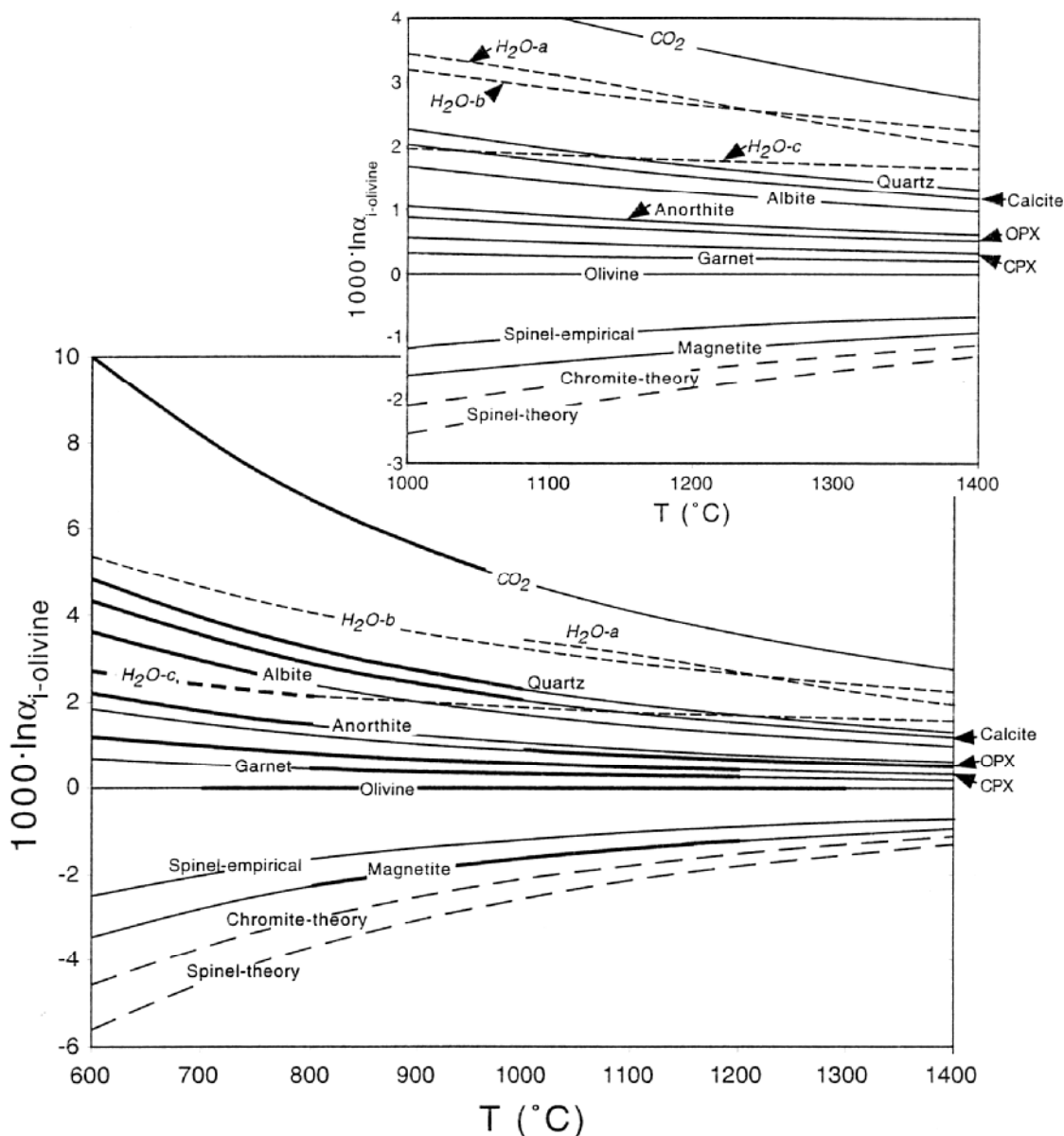
Collectively, these conclusions can be interpreted as meaning that oxygen isotope compositions of primitive basaltic rocks and their mantle sources usually vary within narrow limits and that compositions outside this range, if observed, are most likely caused by sub-solidus alteration or contamination of evolving magmas in the lithosphere. However, several studies suggested that these generalizations are wrong or incomplete, at least with respect to subtle ( $\sim 1$  to 2 per mil) variations in  $\delta^{18}\text{O}$ . For instance, Woodhead et al. (1987) suggested that oceanic arc basalts are systematically  $^{18}\text{O}$ -enriched relative to MORBs due to addition to their sources of components from recently subducted lithosphere. Similarly,  $\sim 0.5$  to 1.0 per mil  $^{18}\text{O}$ -depletions in some ocean-island basalts relative to MORBs were interpreted as a property of their mantle sources, although the cause could not be confidently inferred (Kyser et al. 1982; Harmon and Hoefs 1995). These suggestions did not strongly impact other areas of mantle geochemistry because of the lack of clear and consistent relationships between  $\delta^{18}\text{O}$  and other geochemical properties that are recognized as having significance for whole-earth evolution (e.g. radiogenic isotopes). However, this field has changed in the last six years because a technical innovation—laser-based fluorination (Sharp 1990; Matthey and Macpherson 1993; Valley et al. 1995)—has produced improved records of oxygen isotope variations of mafic and ultramafic rocks. This chapter will particularly emphasize recent observations made using these techniques. It is important to note at the outset that clear records of small oxygen isotope variations in mafic and ultramafic rocks are a relatively new thing; therefore, although detailed interpretations of these records naturally have been put forward, it is likely (perhaps inevitable) that we have yet to understand some of the processes that drive subtle isotopic variations in mantle rocks and basaltic magmas. The following section reviews current knowledge of high-temperature oxygen isotope fractionations among relevant phases and the processes by which they might express themselves.

## ISOTOPIC FRACTIONATIONS RELEVANT TO STUDY OF MANTLE ROCKS AND BASALTIC LAVAS

Oxygen isotope fractionations among silicate melts, their phenocrysts and exsolved gases, and minerals in their residues are small at magmatic temperatures (typically  $\leq 1$  to 2 ‰ for major phases) and can be neglected in studies examining large variations in  $\delta^{18}\text{O}$ , such as those exhibited by some suites of crustally contaminated igneous rocks (e.g. Davidson and Harmon 1989). However, these fractionations are similar in magnitude to the range in  $\delta^{18}\text{O}$  exhibited by relatively primitive, mantle-derived magmas and some fractionations involving minor phases (e.g. oxides,  $\text{CO}_2$ ) can be quite large even at high temperature. Therefore equilibrium isotopic partitioning must be considered when interpreting subtle variations in  $\delta^{18}\text{O}$  typical of basaltic lavas and mantle rocks.

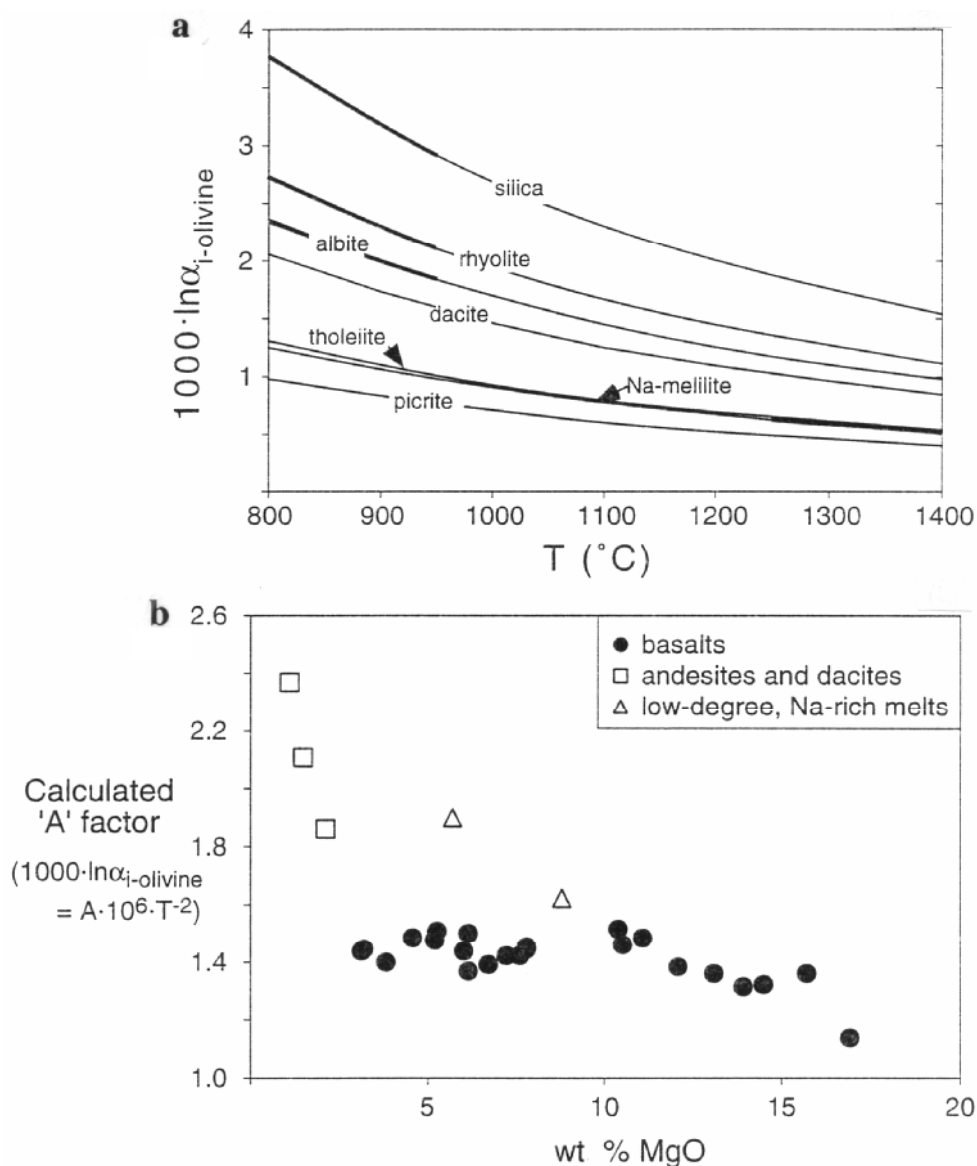
### Experimental, theoretical and empirical constraints on fractionation factors

Figures 1 and 2 summarize select data relevant to discussion of oxygen isotope systematics of mantle rocks and high-temperature silicate liquids and volatiles, shown as plots of the difference in  $\delta^{18}\text{O}$  between a given phase and olivine as a function of temperature. I have chosen olivine as a reference because it is a common early-liquidus



**Figure 1.** Oxygen isotope fractionations among minerals and vapors at mantle temperatures. Thick curve segments mark ranges of direct experimental constraints; thin curve segments are extrapolations or empirical estimates. Long-dash curves are theoretical estimates based on the model of Zheng (1991). Several estimates of the olivine-water fractionation are shown (see text for details); these are emphasized by plotting them as short-dash curves. ‘CPX’ stands for clinopyroxene; ‘OPX’ for orthopyroxene. Natural feldspars should have reduced partition function ratios intermediate between albite and anorthite (in mafic rocks generally near the anorthite extreme). Similarly, natural mantle pyroxenes should be intermediate between CPX and OPX, co-existing natural garnets and clinopyroxenes should be more similar to one another than experiments suggest, and various spinels and Fe-Ti oxides should span a range between magnetite and spinel depending upon their Fe, Cr, Mg, and Al contents (although constraints on this effect are poor).

Fractionations plotted in this figure were calculated based on data from the following references: Experiments from Clayton et al. (1989), Chiba et al. (1989), Rosenbaum and Matthey (1995), Rosenbaum (1994), Rosenbaum et al. (1994a), Matthews et al. (1983), and Matthews et al. (1994); theoretical calculations from Richet et al. (1977), Zheng (1991), and Rosenbaum et al. (1994b); and natural data for mantle peridotites from Chazot et al. (1997). Details of data selection and combination are discussed further in the text.



**Figure 2.** (a) Oxygen isotope fractionations between olivine and various silicate melts at mantle temperatures. Thick curve segments mark ranges of direct experimental constraints; thin curve segments are extrapolations, empirical estimates, or theoretical estimates based on the assumption that fractionation factors for silicate melts equal the weighted sum of those for their normative mineral constituents (taken from Fig. 1). Experimental data in addition to that referenced in Figure 1 come from: Palin et al. (1996), Appora et al. (2000), and Stolper and Epstein (1991). Details of data selection and combination are discussed further in the text. (b) Calculated temperature coefficient, 'A,' for the relationship:  $1000 \cdot \ln \alpha_{i-olivine} = A \cdot 10^6 \cdot T^{-2}$ , based on the assumption that fractionation factors for silicate melts equal the weighted sum of those for their normative mineral constituents and using measured compositions of basaltic and more evolved melts from peridotite partial melting experiments (Baker and Stolper 1994; Baker et al. 1995; Hirschmann et al. 1998), basalt crystallization experiments (Tormey et al. 1987; Juster and Grove 1989), and estimated primary Hawaiian picrite (Hauri 1996).

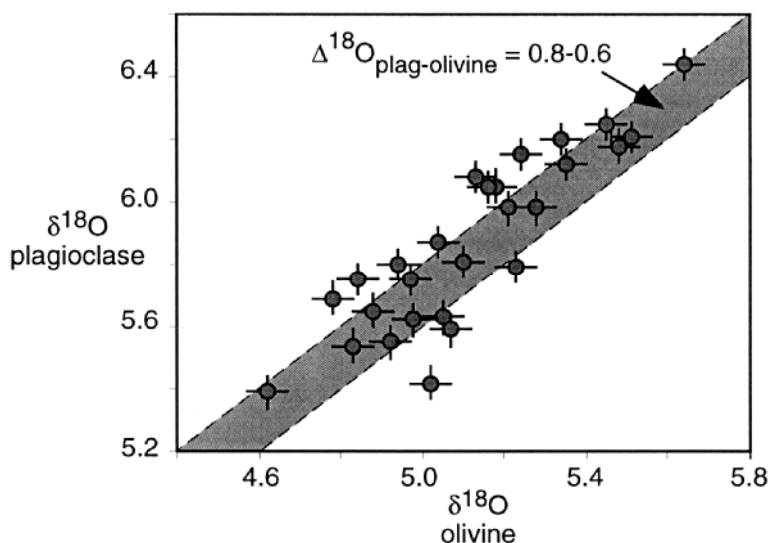
● melts of broadly basaltic composition; □ andesites and dacites produced by high degrees of basalt crystallization; △ Na- and Si-rich, low-degree peridotite melts. Note: all basalts between ~10 and ~3 wt % MgO have similar calculated melt-olivine fractionations.

phase in the crystallization of basaltic melts and the major component of most mantle rocks; furthermore its solid solution is relatively simple, involving only one major exchange component ( $\text{FeMg}^{-1}$ ) that is not thought to impact high-temperature reduced partition function ratios of solids (Kieffer 1982). The plotted curves are calculated as  $1000 \cdot \ln \alpha_{i\text{-olivine}}$ , where  $\alpha_{i\text{-olivine}} = ({}^{18}\text{O}/{}^{16}\text{O})_i / ({}^{18}\text{O}/{}^{16}\text{O})_{\text{olivine}}$ ; these numbers are closely similar to  $\delta^{18}\text{O}_i - \delta^{18}\text{O}_{\text{olivine}}$  unless this difference is large ( $\geq 10$  ‰) or if  $\delta^{18}\text{O}_{\text{olivine}}$  differs greatly from 0 (O'Neil 1986a). In most cases I have had to use informed prejudices to choose among and combine various experimental, theoretical and empirical constraints. The general principle I have used is to adopt the experimental mineral-mineral fractionations of Clayton et al. (1989) and Chiba et al. (1989) wherever possible and to estimate fractionations involving phases not considered in those studies by combining their data with other experiments (preferred) or theoretical or empirical estimates (in last resort). For example, the  $\text{CO}_2$ -olivine fractionation shown in Figure 1 is based on the albite-olivine fractionation reported by Chiba et al. (itself actually a combination of observed albite-calcite and olivine-calcite fractionations) and the  $\text{CO}_2$ -albite fractionation experimentally determined at 1-bar pressure by Matthews et al. (1994). References for this and other fractionations are given in the captions to Figures 1 and 2. This method of combining experimental data sets increases overall uncertainty because of the need to add errors from each experiment in quadrature; I make no effort to present a detailed error analysis here but those using such data in their own work are encouraged to conduct such an analysis on a case-by-case basis. This method of combination is likely to introduce little systematic bias when it involves solid phases examined using similar methods; the potential for error is greater when experiments involving volatile phases at different pressures are combined or extrapolated. In both Figures 1 and 2 thick black curve segments mark the range of direct experimental constraint for each fractionation and thin black curve segments are extrapolations or empirical estimates. Long-dashed curves show estimates based only on theory or (in the case of melt-olivine fractionations) empirical algorithms discussed below. Two sets of estimated fractionations need particular comment:

- (1) Several estimates for the olivine- $\text{H}_2\text{O}$  fractionation are shown; these are emphasized by plotting them as short-dashed curves. One estimate ('a') is taken from Rosenbaum et al. (1994) and is based on combination of theoretical fractionations; a second (curve 'b') combines measured  $\text{CO}_2$ -albite and albite-olivine fractionations (Chiba et al. 1989; Matthews et al. 1994) with the  $\text{CO}_2$ - $\text{H}_2\text{O}$  fractionation calculated by (Richet et al. 1977); the third ('c') combines the albite-water fractionation measured by Matsuhisa et al. (1979) with the albite-olivine fractionation from Chiba et al. (1989). All three of these approaches have their strengths and weaknesses; I will consider the full range of values in the following discussion.
- (2) Estimates of the fractionations between olivine and either spinel or chromite are also problematic; long-dashed curves are based on combining the measured olivine-magnetite fractionation (Chiba et al. 1989) with Zheng's (1991) calculations of fractionations among various metal oxides. However, the curve for the resulting olivine-spinel fractionation is in poor agreement with the sparse data available from studies of mantle xenoliths (Chazot et al. 1997), suggesting a systematic error in one or the other of the constraints combined to make this estimate. Until this discrepancy is resolved, an empirical estimate based on data from Chazot et al. (1997) arguably offers the best constraint. The fine black curve for olivine-spinel fractionations is based on the assumption that olivine-spinel fractionations measured by Chazot et al. in mantle peridotites ( $\sim 1$  per mil) are in isotope exchange equilibrium at the  $\sim 1100^\circ\text{C}$  temperatures suggested by other co-existing oxygen isotope thermometers in those same rocks and scaling of that fractionation with  $T^{-2}$ .

Oxygen isotope fractionations involving silicate melts or glasses (e.g.  $\alpha_{\text{mineral/melt}}$  and  $\alpha_{\text{vapor/melt}}$ ) are poorly known—in fact, I am aware of only two experimentally ‘bracketed’ determinations involving natural melt compositions (Mulenbachs and Kushiro 1974; Palin et al. 1996) and only three ‘bracketed’ determinations involving synthetic melt compositions (Stolper and Epstein 1991; Matthews et al. 1994; Appora et al. 2000); bracketing is the practice of approaching the equilibrium fractionation between two phases from both directions and is generally regarded as a pre-requisite for confident experimental determination (O’Neil 1986b). These data are plotted as a function of temperature in Figure 2; as in Figure 1, all fractionations are relative to olivine and thick segments of those curves mark the range of experimental constraints. Comparison of experimental data in Figures 1 and 2 shows that reduced partition function ratios for silicate glasses and melts are similar to those one would expect for mixtures of minerals in proportion to their normative abundances in those glasses and melts. For example, albite glass is indistinguishable from crystalline albite and rhyolite glass is intermediate to crystalline quartz and albite. However, an important exception to this generalization is the estimated olivine-silica glass fractionation, which is  $\sim 0.3$  ‰ larger than the estimated olivine-quartz fractionation in Figure 1 at a given temperature (Stolper and Epstein 1991). This difference is comparable in magnitude to fractionations between chemically dissimilar minerals at magmatic temperatures (e.g. forsterite-diopside). Nevertheless, there is a general similarity between isotopic fractionations involving experimental melts and those involving minerals with similar cation chemistry. This similarity has been previously noted (Matthews et al. 1994; Palin et al. 1996) and used as the basis for models of fractionation involving melt compositions that have not yet been examined experimentally (e.g. Matthews et al. 1998). These models are generally indistinguishable from the assumption that silicate melts have reduced partition functions equal to the weighted sum of those for their normative mineral constituents. This assumption involves a more familiar translation of melt chemistry than calculations involved in some of the alternative methods (e.g. the ‘Garlick’ index; Matthews et al. 1998), and so I will adopt it throughout this chapter wherever calculated melt-mineral fractionations are discussed. Thin curves in Figure 2 show melt-olivine fractionations calculated by combining this assumption with the data for mineral-olivine fractionations in Figure 1. The fractionation calculated for ‘picrite’ is similar to Matthews et al.’s (1998) model estimate for komatiite; the fractionation calculated for ‘basalt’ is representative of those calculated for a wide range of basaltic and basaltic-andesite compositions. Note also that the model calculation for basalt is quite similar to the experimental determination for Na-melilite—a synthetic basalt analogue. Figure 2b shows the temperature-dependent coefficients for the melt-olivine fractionation of a wide range of natural and experimental melt compositions, calculated using our assumption that melts have fractionation factors similar to the weighted sum of their normative constituents. All values are plotted vs. MgO; a reasonably close estimate of fractionation factors for other basaltic melt compositions can be made by comparison with these results.

There is a large data base of oxygen isotope fractionations measured between phenocrysts and co-existing glass or groundmass in volcanic rocks. It is possible (perhaps likely) that these data are compromised by incorporation of xenocrysts in erupted lavas and sub-solidus alteration of groundmass or glass. Nevertheless, they make up a relatively large data set covering a diverse range in lava chemistry and tectonic setting and therefore typical fractionations observed in these data should offer useful tests of the reasonableness of the experimental, theoretical and empirical estimates described above and summarized in Figures 1 and 2. Figure 3 presents recent data on plagioclase-olivine fractionation in Central American arc lavas, as determined



**Figure 3.** Comparison of oxygen isotope compositions of co-existing olivine and plagioclase in 27 samples of basalt from the Central American volcanic arc. The experimentally-determined range in this fractionation of approximately 0.8 to 0.6 ‰ (assuming  $An_{60-80}$  feldspar, a  $T$  of 1200-1300°C, and data from Chiba et al. 1989) is shown as a gray field with dashed black border. All measurements are unpublished data from the Caltech lab; similar results from smaller suites of samples are presented in Eiler et al. (1995 and 2000a). With few exceptions, data are consistent with a single fractionation near the experimentally determined range.

by laser fluorination in the Caltech laboratories. To the best of my knowledge, this is the largest data set of its type on closely related rocks. The results agree well with the experimental constraints assuming that the plagioclase has an anorthite content of ~60 to 80 mole % (within the range typical of phenocrysts in magnesian arc lavas), suggesting that the data base used to construct Figure 1 provides a reasonably good guide to isotopic partitioning in natural magmatic systems, at least in the case of feldspar-olivine fractionations. There is considerably less laser-based data constraining fractionations between olivine and basaltic glass; most of those data that do exist suggest a melt-olivine fractionation of ~0.4 to 0.5 ‰ (Eiler et al. 2000a), consistent with experiments and model calculations illustrated in Figure 2. However, rigorous experimental constraints on the partitioning of oxygen isotopes between high-temperature minerals or volatiles and melts lag far behind the use of subtle oxygen isotope variations to understand the petrogenesis of such materials. Therefore, laboratory studies of partitioning in these systems are among of the most lasting contributions one could make to this field in the near future.

### Oxygen-isotope systematics of crystallization, partial melting and degassing

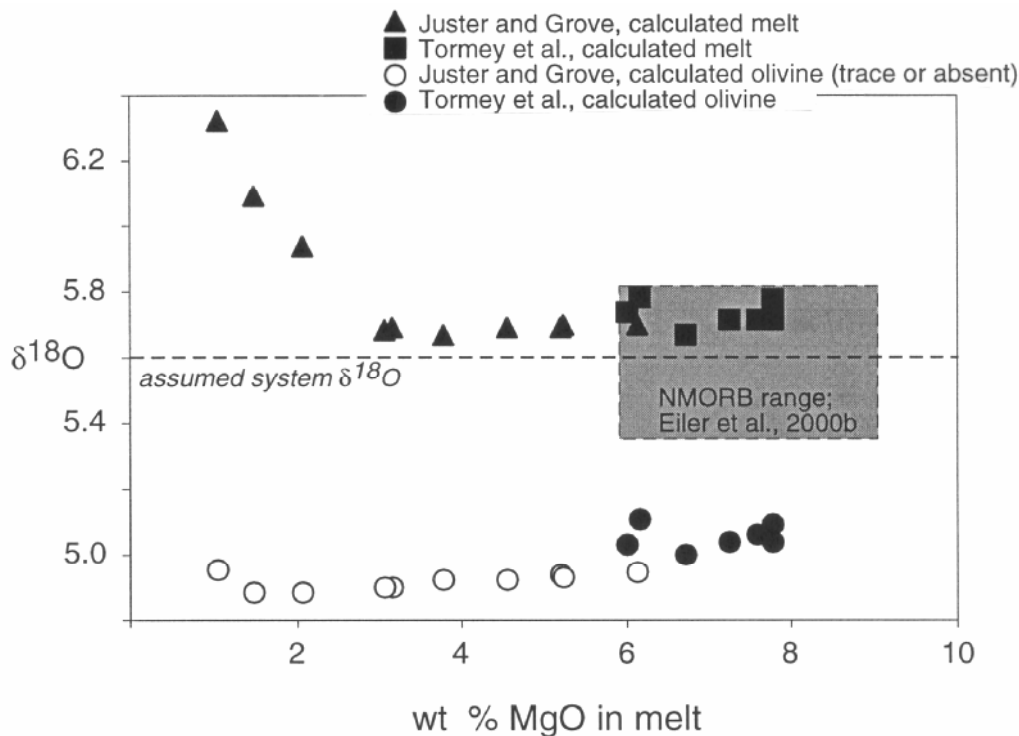
Oxygen isotope fractionations among melts, minerals and magmatic volatiles (Figs. 1 and 2) are large enough to generate observable variations in the  $\delta^{18}O$  of erupted lavas due to crystallization, melting and/or magmatic degassing. These processes have been previously discussed (Matsuhisa et al. 1973; Muehlenbachs and Byerly 1982; Kalamarides 1986; Taylor and Sheppard 1986), but with an emphasis on oxygen isotope changes associated with high extents of differentiation and expressed in highly evolved melts. This section presents models for analogous effects over ranges of relatively



primitive compositions based on data presented in Figures 1 and 2. Most previous models of processes of this sort have assumed that isotopic fractionations among co-existing phases (e.g. melt vs. phenocrysts) always have the same value and then used those fractionations in the equations for equilibrium distribution among co-existing phases or for Rayleigh distillation for certain idealized cases of crystallizing assemblages or melting reactions. What I do here instead is to make one assumption about the nature of melt-mineral fractionations—melts behave as the weighted sums of their normative constituents—and apply that principle in combination with experimental constraints in Figure 1 to calculate the expected isotopic distribution among all co-existing phases in observed assemblages from melting and crystallization experiments. This approach is more work (i.e. one must calculate normative abundances for the melt to estimate its fractionation behavior, calculate mineral-mineral and mineral-melt fractionations at the appropriate temperature, and use the measured modal abundances to calculate the  $\delta^{18}\text{O}$  of each phase for an assumed bulk system  $\delta^{18}\text{O}$ ), and it cannot directly describe the effects of Rayleigh distillation because melting and crystallization experiments generally attempt to produce equilibrium assemblages. However, it has the advantage of correctly describing effects of natural, multiply-saturated melting and crystallization processes and of taking into account temperature- and composition-dependence of fractionations. There are a variety of thermodynamic and empirical models of phase proportions and chemistries in mineral-melt systems (e.g. the ‘Melts’ algorithm of Ghiorso et al. 1994) that could also be used for this purpose; these are not developed here in the interests of simplicity.

### Crystallization

These calculations are based on experimental studies of the equilibrium crystallization sequence of tholeiitic basalt at 1 bar pressure and between 1205 and 1040°C. Two sets of experiments are included: one describing high extents of crystallization of Galapagos basalt (Juster and Grove 1989), dominated by plagioclase and pyroxene crystallization and leading to a pronounced Fe-enrichment trend and very  $\text{SiO}_2$ -rich final liquids, and a second describing lesser extents of crystallization of MORB from the Kane fracture zone (Tormey et al. 1987), dominated by olivine and plagioclase fractionation and producing weaker Fe-enrichment and negligible changes in  $\text{SiO}_2$ . The chosen experiments illustrate the range of behaviors expected of both ‘Fenner’ (Fe-enrichment) and ‘Bowen’ (calc-alkaline) differentiation trends. Calculated melt  $\delta^{18}\text{O}$  values for the first of these are plotted vs. measured melt MgO contents as filled triangles in Figure 4; calculated melt  $\delta^{18}\text{O}$  values for the second set of experiments are shown as filled squares. It is important to note that melt-mineral fractionations are not expected to be constant over the course of basalt crystallization; this is illustrated by also plotting the  $\delta^{18}\text{O}$  of olivine in equilibrium with each calculated melt as circles. Olivine is a major component of the crystallizing assemblage in Kane fracture zone basalt (filled circles) but is present in traces or absent in Galapagos basalt (unfilled circles). Therefore olivine is a ‘fictive’ component in some experiments but is shown for consistency with other figures in this chapter; calculated variations in olivine  $\delta^{18}\text{O}$  values are representative of those for other phenocrysts. In all cases I assume that the entire experimental system (melt plus minerals) has a bulk  $\delta^{18}\text{O}$  of 5.5 ‰. The results of this calculation are that equilibrium crystallization of common basalt compositions will not change the  $\delta^{18}\text{O}$  values of their residual melts by more than ~0.1 ‰ between MgO contents of 8 and 3 wt %. This is principally due to the fact that such basalts are multiply saturated in both higher- $\delta^{18}\text{O}$  and lower- $\delta^{18}\text{O}$  phases (plagioclase and olivine or pyroxene), such that the bulk crystallizing assemblage differs little in  $\delta^{18}\text{O}$  from the melt. For this reason, Rayleigh distillation (i.e. continuous removal of crystals from residual melt) will not appreciably magnify changes in melt  $\delta^{18}\text{O}$  shown in Figure 4



**Figure 4.** Calculated  $\delta^{18}\text{O}$  of silicate melt in equilibrium with co-existing minerals over the course of equilibrium crystallization, plotted vs. measured MgO contents of those melts. Calculated  $\delta^{18}\text{O}$  of co-existing olivine is shown for comparison (other minerals follow patterns similar to olivine and are excluded for simplicity). All calculations are based on measured phase chemistries and proportions in experiments of Tormey et al. (1987) and Juster and Grove (1989), which examine the 1-bar phase equilibria of Galapagos and Kane fracture zone basalts. Calculations assume mineral and melt oxygen isotope fractionation behavior illustrated in Figures 1 and 2; see text for details. Note that the  $\delta^{18}\text{O}$  of melt is nearly constant over a large range in MgO due to ‘buffering’ of  $\delta^{18}\text{O}$  during multiply saturated crystallization; only when residual melt becomes andesitic to dacitic in composition does crystallization generate large changes in melt  $\delta^{18}\text{O}$ . The  $\delta^{18}\text{O}$  values of precipitated minerals are relatively insensitive to equilibrium crystallization. The gray field with dashed black border shows the range in  $\delta^{18}\text{O}$  and MgO contents of NMORB glasses from Eiler et al. (2000b).

except under extreme circumstances. This situation changes for MgO contents less than 2 to 3 wt %, when  $\text{SiO}_2$  contents of the melt become high and  $^{18}\text{O}$  partitions into the melt relative to plagioclase. At this point, melt  $\delta^{18}\text{O}$  can rise sharply (presumably until it begins crystallizing large proportions of quartz). Importantly, the melt-mineral fractionations also change at low MgO contents, such that phenocrysts in equilibrium with these high- $\delta^{18}\text{O}$ , evolved melts will not be significantly different in  $\delta^{18}\text{O}$  from those minerals in equilibrium with more primitive melts of the same source. However, mixing of the most evolved melts with less evolved melts would produce nearly linear mixing curves in Figure 4 and therefore could produce melts with measurable  $^{18}\text{O}$  enrichments at MgO contents of ~3 to 5 wt %. Models of crystallization of magmas with far higher MgO contents than those shown in Figure 4 can be reasonably approximated by Rayleigh distillation of olivine using the picrite-olivine fractionation of ~0.4 ‰. Even highly magnesian melts generally will not crystallize more than 20 to 30 wt % olivine before becoming multiply saturated, and thus the effect of olivine-only fractional crystallization will generally be  $^{18}\text{O}$ -enrichments of residual melt by amounts 0.1 ‰.

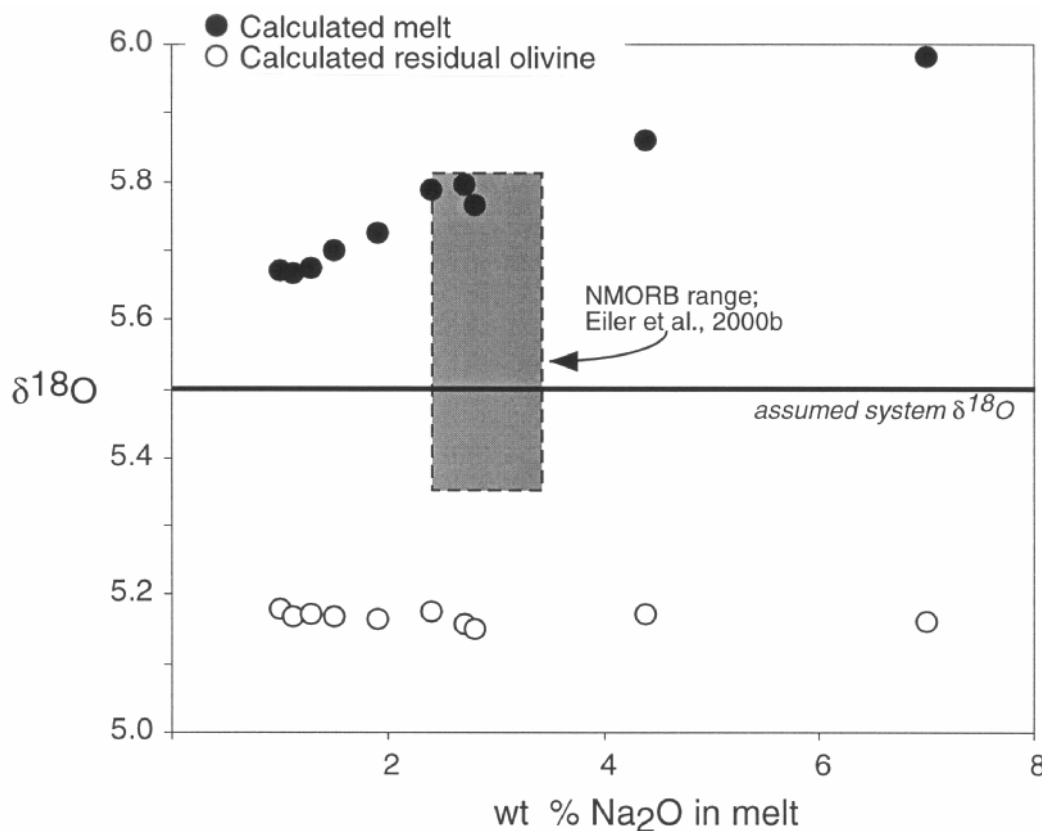
For comparison, the gray field in Figure 4 shows the range in  $\delta^{18}\text{O}$  and MgO for NMORB glasses recently examined by Eiler et al. (2000b);  $\delta^{18}\text{O}$  is uncorrelated with MgO in this suite and varies by more than can be accounted for by low-pressure crystallization alone. I am aware of no high-precision data sets of significant size that clearly document changes in  $\delta^{18}\text{O}$  with increasing extent of differentiation among basalts and basaltic andesites, perhaps because such studies have generally focused on the samples with 6 to 9 wt % MgO in which these effects are expected to be small ( $\sim 0.1$  ‰). However, several studies document increases in  $\delta^{18}\text{O}$  with increasing extent of differentiation among components of layered basic intrusions (Kalamarides 1986) and evolved lavas (Matsuhisa et al. 1973; Muehlenbachs and Byerly 1982) that are generally consistent with the size and direction of changes in melt  $\delta^{18}\text{O}$  illustrated in Figure 4.

### Partial melting

This section describes the results of a model calculation that follows the same methods and assumptions described above (i.e. mineral proportions and melt chemistries are taken from experiments and mineral-melt fractionations are based on assumptions described with reference to Fig. 2) but applies them to experiments examining partial melting of fertile spinel peridotite at 10 kbar and temperatures of 1390 to 1250. The experiments considered used the ‘diamond aggregate’ method (Baker and Stolper 1994; Baker et al. 1995; Hirschmann et al. 1998) and extend to very low melt fractions (1.4 %) where melts are enriched in Na and Si compared to typical basalts. The results of these experiments are controversial because of the unusual compositions of the lowest-temperature melts, but they are useful for this purpose because they provide an extreme case of oxygen isotope variations that might be produced by peridotite partial melting. The empirical model of olivine-spinel fractionations in Figure 1 (thin black curve) was used to calculate the effects of changing oxide abundances in solid residues. As with the preceding calculations, co-existing minerals and melts are assumed to be in isotopic equilibrium with one another at all times. This is a reasonable assumption for a model of this type, although some studies of mantle peridotites have suggested that fluid-rock and/or melt-rock interaction may take place under local disequilibrium conditions (Zhang et al. 2000).

The results of this calculation are shown in Figure 5 as a plot of the calculated  $\delta^{18}\text{O}$  of melt and olivine in the residual peridotite as a function of the measured  $\text{Na}_2\text{O}$  content of the melt—a useful and widely used indicator of the extent of melting of mantle rocks (e.g. Langmuir et al. 1992). The range in measured  $\delta^{18}\text{O}$  and fractionation-corrected  $\text{Na}_2\text{O}$  in NMORBs (‘ $\text{Na}_{8.0}$ ’ of Langmuir et al. 1992— $\text{Na}_2\text{O}$  content corrected to 8.0 wt % MgO) is shown for comparison (Eiler et al. 2000b);  $\delta^{18}\text{O}$  and  $\text{Na}_2\text{O}$  are uncorrelated in this suite. Our model calculations predict that the  $\delta^{18}\text{O}$  of partial melts of upper-mantle rocks could vary by up to 0.3 ‰ due to melting processes alone, increasing approximately linearly with increasing  $\text{Na}_2\text{O}$  as melt fraction decreases from  $\sim 30$  to  $\sim 1$  %; the  $\delta^{18}\text{O}$  values of residual minerals are predicted to be relatively constant ( $< 0.1$  ‰ range). This effect is principally due to increasing abundance of ‘albite’ component in the melt with decreasing melt fraction. However, most of the calculated range in  $\delta^{18}\text{O}$  is expressed only in melts with unusual compositions; for  $\text{Na}_2\text{O}$  contents of 2 to 4 wt % (the range typical of oceanic tholeiites), a range in  $\delta^{18}\text{O}$  of only 0.1 ‰ is predicted. Because the predicted relationship between  $\delta^{18}\text{O}$  and  $\text{Na}_2\text{O}$  is nearly linear, mixing of partial melts (for instance, due to ‘dynamic melting’ processes thought to be important for MORB melting; Langmuir 1992) cannot magnify (or decrease) this effect. The  $\text{Na}_2\text{O}$  contents of NMORBs examined by Eiler et al. (2000b) span too small a range for this effect to account for their variations in  $\delta^{18}\text{O}$ .

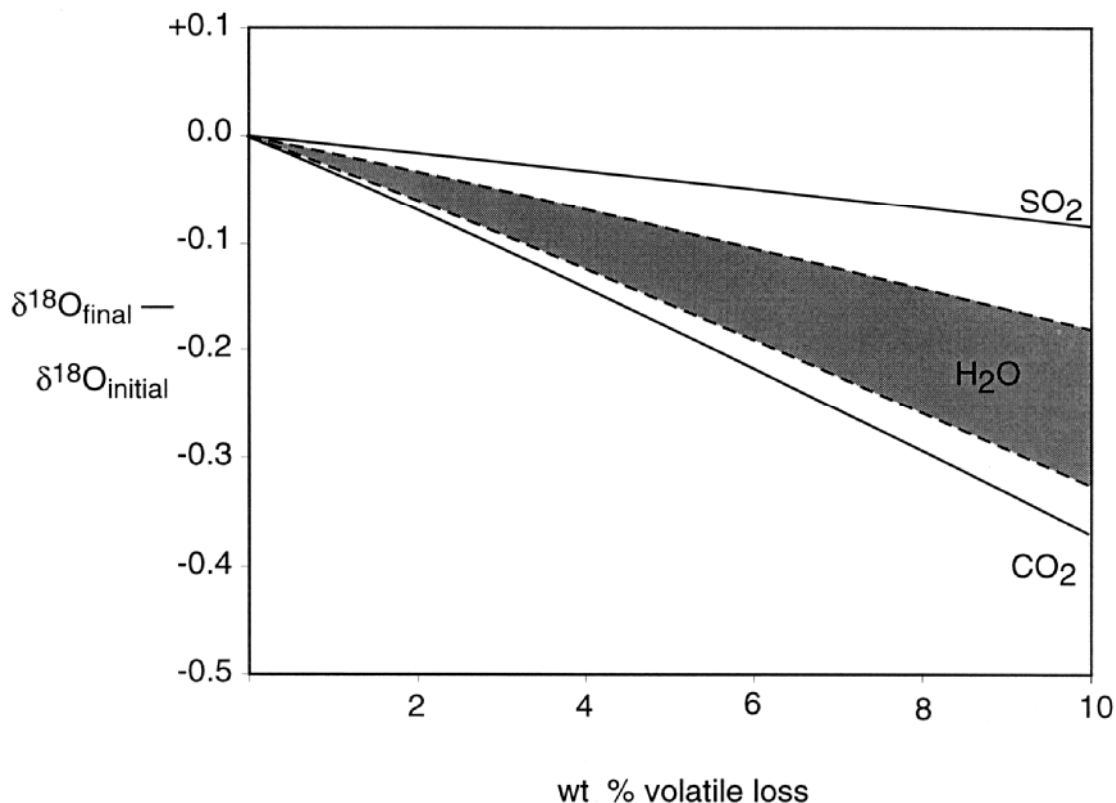
Note that at very low degrees of melting ( $< 1$  %) melts of metasomatized or mafic



**Figure 5.** Calculated  $\delta^{18}\text{O}$  of silicate melt in equilibrium with co-existing minerals during ‘batch’ melting of peridotite, plotted vs. measured  $\text{Na}_2\text{O}$  contents of those melts. Calculated  $\delta^{18}\text{O}$  of co-existing olivine is shown for comparison (other minerals follow patterns similar to olivine and are excluded for simplicity). All calculations are based on measured phase chemistries and proportions in experiments of Baker and Stolper (1994), Baker et al. (1995) and Hirschmann et al. (1998), which examine the phase equilibria of partially molten synthetic spinel peridotite. Calculations assume mineral and melt oxygen isotope fractionation behavior illustrated in Figures 1 and 2; see text for details. Note that the  $\delta^{18}\text{O}$  of partial melt increases linearly with increasing  $\text{Na}_2\text{O}$  due to increasing ‘albite’ component of partial melt with decreasing melt fraction; however, common tholeiitic basalts having 2-4 wt %  $\text{Na}_2\text{O}$  are expected to vary little in  $\delta^{18}\text{O}$  due to this effect. The  $\delta^{18}\text{O}$  values of residual minerals are insensitive to the extent of batch melting. The gray field with dashed black border shows the range in  $\delta^{18}\text{O}$  and  $\text{Na}_2\text{O}$  contents of NMORB glasses from Eiler et al. (2000b).

mantle rocks may be strongly enriched Na, Si and perhaps other components ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{SO}_2$ ) and therefore even more extreme in their oxygen isotope compositions than the Na-rich end in Figure 5. Carbonatitic, rhyolitic and dacitic liquids in equilibrium with average mantle olivine should have  $\delta^{18}\text{O}$  values of  $\sim 7$  to  $8$  ‰—approximately 1 to 2 ‰ higher than basaltic high-degree melts of those same sources (Fig. 2). However, these exotic melts will also have unusual isotopic fractionations with respect to their precipitated phenocrysts; e.g. the first olivine to precipitate from a chemically exotic melt should be, to first order, equal in  $\delta^{18}\text{O}$  to olivine in the mantle source of that magma. Therefore, isotopic fractionations of this type should not be expressed in the oxygen isotope variability of phenocrysts except under special circumstances. There are currently no strong observational constraints on the variation in  $\delta^{18}\text{O}$  of partial melts of mafic or ultramafic rocks with variations extent of melting of a source that can be reasonably inferred to be constant in  $\delta^{18}\text{O}$  (studies of arc-related rocks suggest such a relationship, but these effects are inconsistent with those discussed here and have a

different interpretation discussed below). Eiler et al. 1996a, report oxygen isotope compositions of olivines and pyroxenes from extremely depleted harzburgites from the Voykar ophiolite, Russia which are interpreted to be residues of high degrees of melting in a ridge environment. These rocks are indistinguishable in  $\delta^{18}\text{O}$  from average mantle peridotites (Mattey et al. 1994), consistent with the calculations illustrated in Figure 5.



**Figure 6.** Calculated change in  $\delta^{18}\text{O}$  of basaltic melt as a function of volatile loss (in wt. %). This calculation assumes that the conditions for Rayleigh distillation apply, olivine-volatile fractionations shown in Figure 1, a  $\text{CO}_2\text{-SO}_2$  fractionation given by Richet et al. (1977), an olivine-melt fractionation of 0.5 per mil, and a temperature of  $1200^\circ\text{C}$ . A range of water-melt fractionations were used (short-dash curves in Fig. 1), leading to a range of predicted isotopic effects of de-watering. Note that the  $\delta^{18}\text{O}$  of the initial magma likely depends on initial volatile content (i.e.  $\text{CO}_2$ -rich melts might be higher in  $\delta^{18}\text{O}$  than  $\text{CO}_2$  poor melts equilibrated with the same residual mantle minerals); this effect will tend to make degassed but initially volatile-rich melts more similar to melts that were always volatile poor than suggested by this calculation.

### Devolatilization

Oxygen isotope changes during degassing of basalts are generally neglected because the volatile contents of submarine glasses are so low that even complete degassing should be incapable of producing large shifts in  $\delta^{18}\text{O}$ . However, these changes could be non-trivial in special cases (e.g. dehydration of water-rich melts in subduction zone environments; Sisson and Layne 1993) and therefore they are a potential source of oxygen isotope variability in erupted silicate melts. This section presents a relatively simple, idealized model in which the  $\delta^{18}\text{O}$  of residual melt is calculated as a function of the wt % of various volatiles lost assuming a constant melt-volatile fractionation for each species. Figure 6 presents the expected change in  $\delta^{18}\text{O}$  of a basaltic melt during

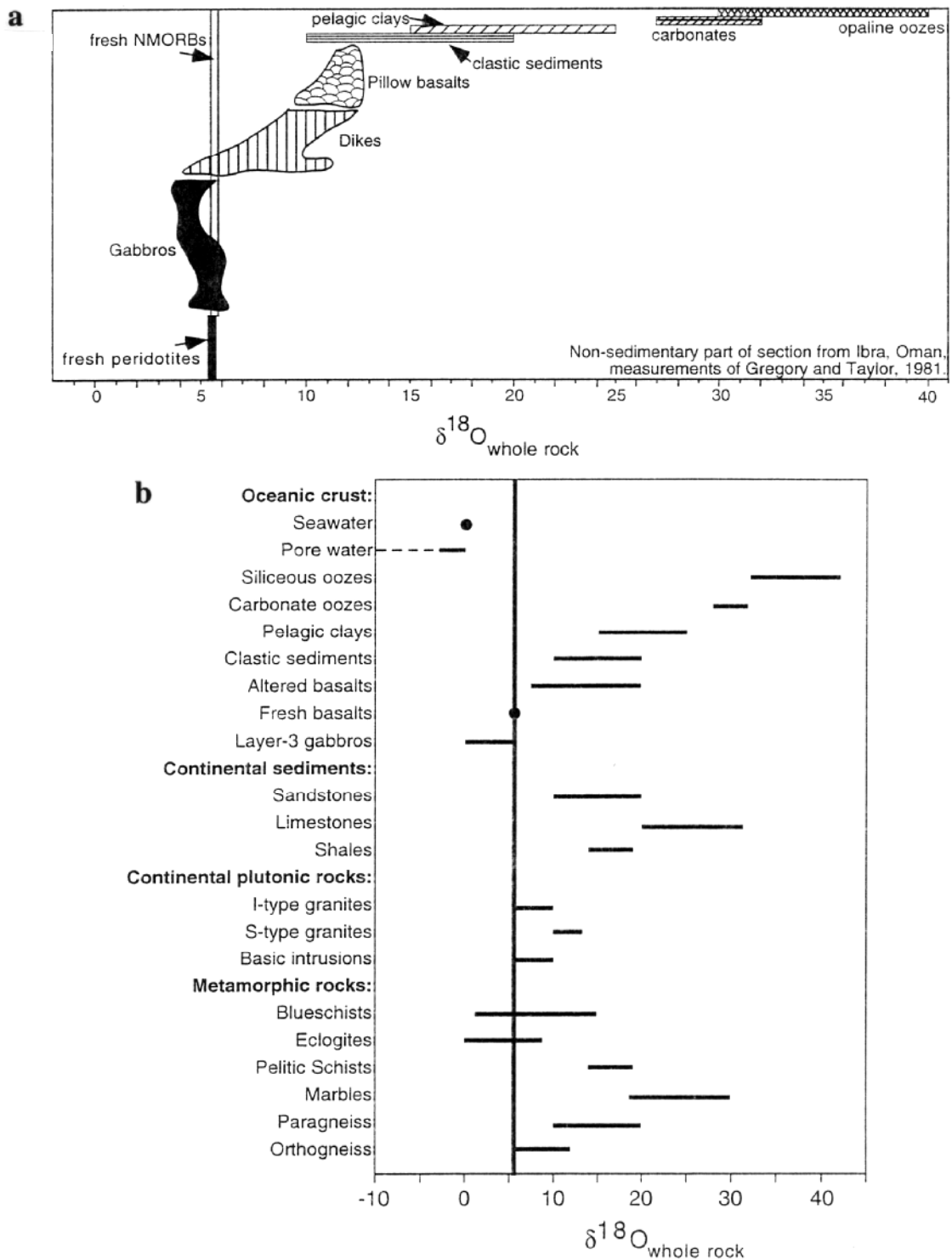
degassing of H<sub>2</sub>O, CO<sub>2</sub> and SO<sub>2</sub>. Losses of reduced gasses such as H<sub>2</sub>, H<sub>2</sub>S and CH<sub>4</sub> obviously have no direct effect on the  $\delta^{18}\text{O}$  of residual melt, although it is possible that they could have indirect effects such as driving fractional crystallization of oxides which in turn change the  $\delta^{18}\text{O}$  of residual melt. All curves assume Rayleigh distillation and melt-vapor fractionation factors cited in the caption ('batch' devolatilization will have similar effects over the plotted range in extents of degassing; Valley 1986); a range of melt-water fractionations were assumed to capture the range of possible effects implied by diverse experimental and theoretical constraints (Figs. 1 and 2). Degassing of H<sub>2</sub>O, CO<sub>2</sub> and SO<sub>2</sub> over the range of abundances for those species in most submarine basalts (0 to 1 wt % H<sub>2</sub>O; 0 to 0.1 wt % CO<sub>2</sub>; 0 to 0.3 wt % SO<sub>2</sub>) should produce variations in  $\delta^{18}\text{O}$  that are small relative to analytical precision and the natural variability of basaltic rocks (< 0.1 ‰). The same should be true of SO<sub>2</sub> degassing from even strongly sulfate-enriched melts. However, the expected shift in  $\delta^{18}\text{O}$  due to degassing of CO<sub>2</sub>-rich melts and, under some assumptions of melt-water fractionation, H<sub>2</sub>O-rich melts can be many times analytical precision. Arc-related lavas in particular are suspected in some cases of being descended from primary melts with many wt % of dissolved H<sub>2</sub>O (Sisson and Layne 1993) and therefore there is reason to suspect that devolatilization alone could promote the generation of <sup>18</sup>O-depleted convergent-margin lavas (~0.2 to 0.3 per mil lower than basalt in equilibrium with their mantle sources). The initial CO<sub>2</sub> abundances required for similar extents of magma <sup>18</sup>O depletion (>1 to 2 wt %) are higher than those believed likely based on current constraints on the volatile contents of tholeiitic basalts (Holloway and Blank 1994); however, the primary CO<sub>2</sub> contents of mantle melts are not well known and in some cases might be very high (Wyllie 1996); therefore this effect could be important in some settings.

## **ISOTOPIC SIGNATURES OF CRUSTAL CONTAMINANTS AND SUBDUCTED LITHOSPHERE**

Although issues of high-temperature isotopic fractionation discussed in the preceding sections are important for interpreting variations in  $\delta^{18}\text{O}$  of basaltic lavas and mantle rocks (and may become increasingly important as our understanding of these fractionations improves), the principle motivation for studying oxygen isotope variations in such samples is to detect and characterize subducted crustal components in the mantle and/or crustal contaminants that have influenced magmatic differentiation. This section describes the known isotopic variability of crustal rocks and sediments and their inferred subducted equivalents; Figures 7a and 7b summarize these data. This section can only briefly summarize the great deal of relevant data; interested readers are encouraged to read review articles cited below for further information.

### **Oceanic crust and sediments**

It is generally believed that most of the crustal material injected into the asthenosphere and deeper mantle comes from the sediments and altered basaltic and gabbroic components of the subducted oceanic lithosphere (Hofmann 1997), although delamination of deep crustal plutonic rocks may also provide a major source of recycled crust (Kay and Kay 1993; Ducea and Saleeby 1998). The oxygen isotope composition of old oceanic crust and underlying lithospheric mantle is complex and portions of it are only known by studying ophiolites, which may not be representative of the ocean floor generally. Nevertheless, the following generalizations appear to be robust: Phanerozoic oceanic carbonate sediments have  $\delta^{18}\text{O}$  values of 25 to 32 ‰, siliceous oozes 35 to 42 ‰, and pelagic clays 15 to 25 ‰ (Kolodny and Epstein 1976; Arthur et al. 1983); weathered and hydrothermally altered upper oceanic crust generally has  $\delta^{18}\text{O}$  values of 7 to 15 ‰ and hydrothermally altered lower oceanic crustal gabbros 0 to 6 ‰ (Gregory and



**Figure 7.** (a) Idealized oxygen isotope profile of altered, sediment-covered oceanic crust; based on Gregory and Taylor's (1981) study of the Ibra section of the Oman ophiolite and data for marine sediments taken from data sources cited in the text. The vertical black bar marks the range in  $\delta^{18}\text{O}$  typical of mantle peridotites; the vertical white bar marks the range in  $\delta^{18}\text{O}$  typical of fresh oceanic basalts. (b) Values of  $\delta^{18}\text{O}$  typical of various major rock types in the Earth's crust. Data sources are listed in the text. These ranges emphasize typical, representative values and purposefully exclude extreme examples of many rock types. The isotopic composition of most mantle peridotites (Fig. 8) and all NMORBs (Fig. 9) spans a range equal to the thickness of the vertical black line.

Taylor 1981; Alt et al. 1986; Muehlenbachs 1986; Stakes 1991; Staudigel et al. 1995; see Fig. 7a). It is also worth noting that pore-waters in the oceanic crust are initially low in  $\delta^{18}\text{O}$  (0 near the sediment-water interface to -3 ‰ at depths of several hundred meters; Perry et al. 1976), although it would be reasonable to assume that these waters are quantitatively expelled and/or isotopically equilibrated with co-existing rocks before the oceanic lithosphere is deeply subducted. Because lower crustal gabbros (and pore fluids) on one hand and upper crustal basalts and sediments on the other deviate in  $\delta^{18}\text{O}$  from typical peridotites ( $\delta^{18}\text{O} = 5.5 \pm 0.2$ ; detailed below) in opposite directions, the oxygen isotope system has the potential to discriminate between subducted components derived from different parts of the oceanic crust. Of course, it is also possible that a mixture of ocean crust components could balance to have no contrast in  $\delta^{18}\text{O}$  with the mantle. However, this case would require fortuitous mixtures of these materials and is not to be generally expected.

### **Subduction-zone metamorphic rocks**

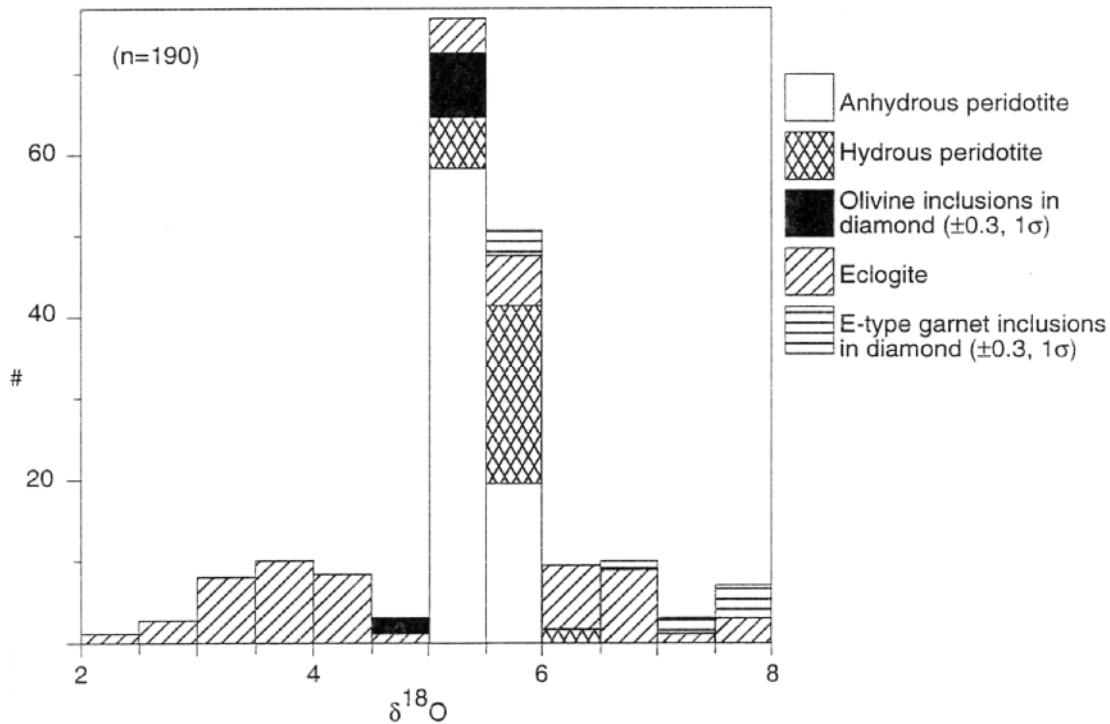
Subduction of oceanic lithosphere produces profound changes in its chemistry, principally because volatiles and their dissolved solutes are driven off during metamorphic reactions, and in some cases due to partial melting of the 'slab'. Several lines of evidence indicate that these processes have little impact on the bulk  $\delta^{18}\text{O}$  of thick sections (10's of meters or thicker) of subducted oceanic crust, although they can homogenize meter-scale and smaller oxygen-isotope contrasts between adjacent rocks. The best evidence comes from studies of blueschist and eclogite facies metamorphic terrains (e.g. Bebout and Barton 1989; Putlitz et al. 2000), which document that deeply subducted oceanic crust retains both  $^{18}\text{O}$ -enriched and  $^{18}\text{O}$ -depleted components, each with  $\delta^{18}\text{O}$  values and in relative proportions broadly similar to those in unsubducted oceanic crust. Additional constraints that lead to the same conclusion come from studies of eclogite xenoliths and mantle xenocrysts believed to be related to recycled crust (Garlick et al. 1971; Neal et al. 1990; Nadeau et al. 1993; Valley et al. 1998), mafic rocks associated with alpine peridotites (Pearson et al. 1991), and eclogite-type inclusions in mantle diamonds (Lowry et al. 1999), although this last suite of materials is not known to include  $^{18}\text{O}$ -depleted compositions. A subset of these data are shown in Figure 8 along with data for mantle peridotites, which are discussed below.

It was recently discovered that ultra-high-pressure metamorphic complexes in northeast China contain mafic metamorphic rocks—plausibly deeply subducted basalts—with some of the lowest  $\delta^{18}\text{O}$  values ever observed in terrestrial rocks (down to -10 ‰; Yui et al. 1995). These values can be interpreted as a result of high-temperature hydrothermal alteration by low- $\delta^{18}\text{O}$ , perhaps high-latitude, meteoric waters before subduction. In this case, these  $\delta^{18}\text{O}$  values are an historical accident unrelated to the extreme tectonic processes the rocks subsequently underwent and are likely not representative of recycled crustal materials.

### **Upper continental crust**

The oxygen isotope geochemistry of the upper continental crust is dominated in most cases by the relative proportions of carbonate and siliciclastic sediments ( $\delta^{18}\text{O} = 20$  to 30 ‰ and 10 to 20 ‰, respectively; Kolodny and Epstein 1976; Arthur et al. 1983) and granitoids ( $\delta^{18}\text{O} = 7$  to 14, with higher values systematically observed in those generated by melting pre-existing sediments; Taylor 1968; Taylor and Sheppard 1986), or their metamorphosed equivalents. I am not aware that anyone has estimated the globally-averaged  $\delta^{18}\text{O}$  of the upper continental crust (beyond broad approximations). Such an estimate would require a careful inventory of the relative proportions of the relevant rock types and is beyond the scope of this work. However, the most important





**Figure 8.** Oxygen isotope compositions of representative mafic and ultramafic mantle xenoliths. All data are reported on a whole-rock basis where possible and as named minerals when necessary; however, fractionations among co-existing minerals are small ( $\leq 0.5$  ‰) in most cases and introduce no significant bias at the scale plotted. Note that all ultramafic rock types span a small range in  $\delta^{18}\text{O}$  centered around  $\sim 5.5$  ‰; eclogites and ‘E-type’ inclusions in diamonds span much greater ranges, presumably reflecting a relationship to subducted oceanic crust. Data sources: Garlick and MacGregor (1971), Ongley et al. (1987), Neal et al. (1990), Kempton et al. (1988), Fourcade et al. (1994), Matthey et al. (1994), Chazot et al. (1997), and Lowry et al. (1999).

point to consider for studies of  $\delta^{18}\text{O}$  values in basalts that have interacted with continental crust is the makeup of the local crustal section: Cratonic margins and mobile belts rich in clastic and (particularly) chemical sediments will tend to be high in  $\delta^{18}\text{O}$ , whereas cratonic cores of plutonic rocks and mobile belts rich in juvenile igneous rocks will tend to be closer to mantle  $\delta^{18}\text{O}$  values. An example of this difference can be seen in the difference in oxygen isotope composition between crustally-derived granitoids in the Grenville province (high  $\delta^{18}\text{O}$ ; metasediment-rich mobile belt) on one hand and the Superior province (low  $\delta^{18}\text{O}$ , orthogneiss-rich craton) on the other (Peck et al. 2000).

### Lower continental crust

The oxygen isotope geochemistry of the lower continental crust depends principally on the relative proportions of juvenile plutonic rocks (i.e. those produced from basaltic underplating) on one hand and tectonically emplaced upper-continental crustal rocks on the other. The first of these are best represented by mafic xenoliths from depths of 30 to 50 km (granulites and eclogites) whereas the latter are arguably best represented by regional granulite facies terrains, most of which sample the middle of doubly-thickened orogenic crust (Harley 1989). The oxygen isotope geochemistry of deep-crustal orthogneisses and paragneisses is reviewed by Valley (1986); tectonically emplaced sediments, granitoids and their metamorphosed equivalents are, to first order, similar to their upper-crustal progenitors described above. Clemens-Knott (1992) reports studies of the oxygen isotope geochemistry of the interface between juvenile plutonic lower crust and pre-existing metamorphic lower crust in the Sierra Nevada and Ivrea zone. The most

primitive members of juvenile plutonic rocks in these settings have  $\delta^{18}\text{O}$  values close to those typical of upper mantle rocks and oceanic basalts (i.e.  $\delta^{18}\text{O} = 6$  to  $7$  ‰). However, parts of the plutonic complex in the Ivrea zone are subject to extensive contamination by stopped blocks and partial melts of the pre-existing crustal rocks they intrude and can take on  $\delta^{18}\text{O}$  values of  $8$  to  $10$  ‰ due to this pollution. Kempton and Harmon (1992) provide the most extensive available study of the oxygen isotope geochemistry of deep-crustal xenoliths, showing that plutonic complexes intruded into the base of the continental crust generally undergo extensive interaction with pre-existing metasediments and felsic igneous rocks, resulting in large (several per mil)  $^{18}\text{O}$ -enrichments of mafic granulites compared to upper mantle rocks and oceanic basalts.

### OXYGEN ISOTOPE COMPOSITIONS OF MANTLE PERIDOTITES

The oxygen isotope geochemistry of mantle peridotites was until recently a controversial subject (Kyser et al. 1981; Gregory and Taylor 1986). Many conventional fluorination measurements indicated that pyroxenes in most upper-mantle rocks span a relatively narrow range in  $\delta^{18}\text{O}$  ( $\sim 1$  ‰) whereas olivines in those same rocks span a much larger range ( $\sim 3$  ‰) that is uncorrelated with the  $\delta^{18}\text{O}$  of coexisting pyroxenes (Kyser et al. 1981). This result was interpreted as either a consequence of complex temperature dependence to the olivine-pyroxene fractionation (Kyser et al. 1981) or of differences between olivine and pyroxene in the rate of isotopic exchange with metasomatizing fluids and/or melts (Gregory and Taylor 1986). In either case, the implication was that the oxygen isotope compositions of upper mantle rocks are usually variable and internally complex. Other studies suggested that olivine, garnets and pyroxenes are generally in mutual oxygen isotope equilibrium, but still vary by approximately 2 to 3 per mil from sample to sample (Harmon et al. 1986).

Subsequent study of peridotites (including many of the same samples investigated by Kyser et al. 1981) using laser fluorination techniques contradicts much of these earlier data, instead showing that most mantle peridotites span a relatively narrow range in  $\delta^{18}\text{O}_{\text{whole-rock}}$  ( $5.5 \pm 0.2$  ‰) and almost universally consist of minerals that are in mutual oxygen isotope equilibrium predicted by experimental constraints (Mattey et al. 1994; Ionov et al. 1994; Chiba et al. 1989). The scope of Mattey et al.'s (1994) survey of mantle peridotites and the internal consistency of their results suggests that the complexity apparent in earlier studies is an artifact of low analytical yields in conventional fluorination of refractory minerals and that the upper mantle principally consists of peridotites of nearly fixed and internally equilibrated oxygen isotope composition. This conclusion is re-affirmed by a subsequent comparison of hydrated (i.e. amphibole-bearing) and anhydrous mantle peridotites (Chazot et al. 1997), which found them to be indistinguishable in  $\delta^{18}\text{O}$  from one another and from typical mantle peridotites previously analyzed by Mattey et al (1994). These data are summarized in Figure 8 along with the compositions of mantle eclogites and 'E-type' inclusions in diamonds. A dissenting view that re-interprets the Kyser et al. (1981) results was presented by Rosenbaum et al. (1994a). Finally, it should be noted that most of the mantle peridotites that have been measured for  $\delta^{18}\text{O}$  come from the continental lithospheric mantle and thus may be unrepresentative of the mantle as a whole.

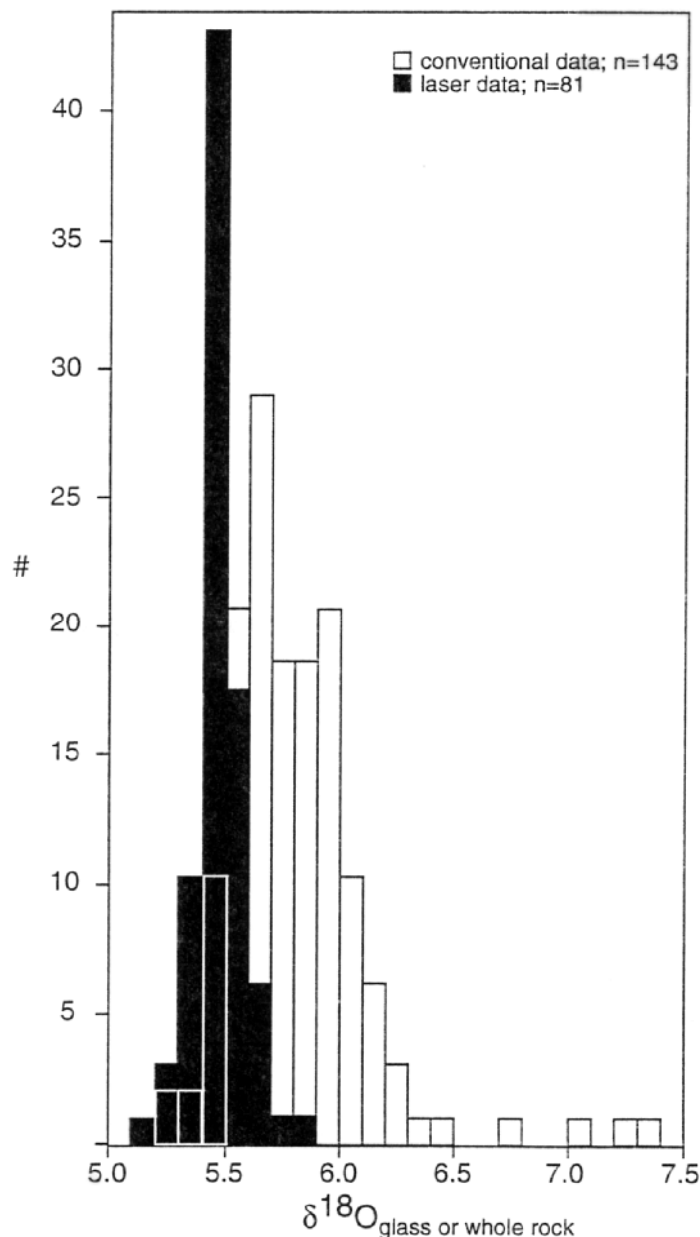
More recently there have been several indications that the oxygen isotope geochemistry of mantle xenoliths from certain exotic settings can be more variable than indicated by Mattey et al.'s (1994) survey and subsequent work of Chazot et al. (1997). Zhang et al. (2000) present oxygen isotope measurements on variably metasomatized and re-crystallized ultramafic xenoliths from the Kaapvaal craton, South Africa, which document inter-mineralic disequilibrium and intra-crystalline zonation that presumably

reflect metasomatic fluid-rock interaction. The direction of these changes is toward  $^{18}\text{O}$ -depletions in the most metasomatized portions of the rocks. Similarly, Deines and Haggerty (2000) report complex intra-crystalline zonation in the oxygen isotope compositions of ultramafic xenoliths thought to come from unusually great depths. Finally, Valley et al. (1998) interpret variability in  $\delta^{18}\text{O}$  among some zircon metacrysts in kimberlites as a consequence of recycling of subducted material into mantle melts. Collectively, these results suggest that there are discoveries to be made in the oxygen isotope geochemistry of metasomatized ultramafic xenoliths; nevertheless, it is important to keep in mind that such samples are rare.

Additional insight about the oxygen isotope geochemistry of the earth's mantle comes from lunar rocks, which sample a system that plausibly began its evolution with an oxygen isotope composition like that of the earth but has differentiated without weathering, hydrothermal alteration or subduction (although contamination of lunar magmas by the regolith could potentially influence their oxygen isotope compositions). Only one study has examined the  $\delta^{18}\text{O}$  of lunar rocks using laser-based techniques (Wiechert et al. 2000), but much of the conventional data generated in response to the Apollo program was of unusually high quality and was not affected by the post-eruptive weathering that compromises whole-rock analyses of terrestrial volcanic rocks (Onuma et al. 1970; Clayton et al. 1971; Clayton et al. 1972; Clayton and Mayeda 1996). Results of both laser-based and conventional studies indicate that lunar anorthosites and minerals and glass in most lunar basalts span a narrow range in  $\delta^{18}\text{O}$  that is close to high-temperature equilibrium with the average value for terrestrial MORBs (detailed below); this result supports the view that the earth's upper mantle is within  $\sim 0.1$  to  $0.2$  ‰ of its primordial  $^{18}\text{O}/^{16}\text{O}$  ratio. There is, however, one remarkable exception: Wiechert et al. (2000) found several high-Ti lunar basalts that are  $^{18}\text{O}$ -depleted by several tenths of per mil relative to most lunar and terrestrial basalts. This observation was attributed to re-melting of Fe-Ti-oxide cumulates in the lunar upper mantle, which could be low in  $\delta^{18}\text{O}$  because of high-temperature isotopic fractionations between Fe-Ti oxides and common silicates and silicate melts (Fig. 1). It should also be noted that the analyzed glasses are far richer in FeO and  $\text{TiO}_2$  and poorer in  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  than the terrestrial and lunar basalts to which they are compared; therefore their  $^{18}\text{O}$ -depleted compositions could also reflect their unusual fractionations relative to minerals in their residues (Fig. 2) rather than their extraction from a low- $\delta^{18}\text{O}$  source. This second hypothesis will be difficult to evaluate without experimental constraints on fractionation factors involving melts having such exotic major element compositions.

### MID-OCEAN RIDGE BASALTS

Mid-ocean-ridge basalts (MORBs) are the most abundant and widespread terrestrial magmas and span relatively small ranges in composition for many geochemical indices (e.g. Sr isotope ratios; Hofmann 1997); therefore they are a natural reference frame for defining the geochemical properties of the upper mantle. Early studies of the oxygen isotope geochemistry of MORBs established that they span a limited range in  $\delta^{18}\text{O}$  (generally  $\sim 5$  to  $7$  per mil;  $\square$  in Figure 9; see figure caption for references) and, as mentioned above, have an average value that is near those for mafic lunar rocks. For these reasons, and in light of the complexity of oxygen isotope variations believed at that time to be characteristic of terrestrial peridotites, MORBs were widely used to define the  $\delta^{18}\text{O}$  value of the earth's mantle. This interpretation of the oxygen isotope geochemistry of MORBs was re-enforced by the study of Ito et al. (1987)—until recently the most extensive and systematic survey of the oxygen isotope composition of any one major class of terrestrial basalts. Ito et al. (1987) found that fresh MORB glasses vary in  $\delta^{18}\text{O}$  between  $5.3$  and  $6.2$  ‰, but that most fall within the range  $5.5$  to

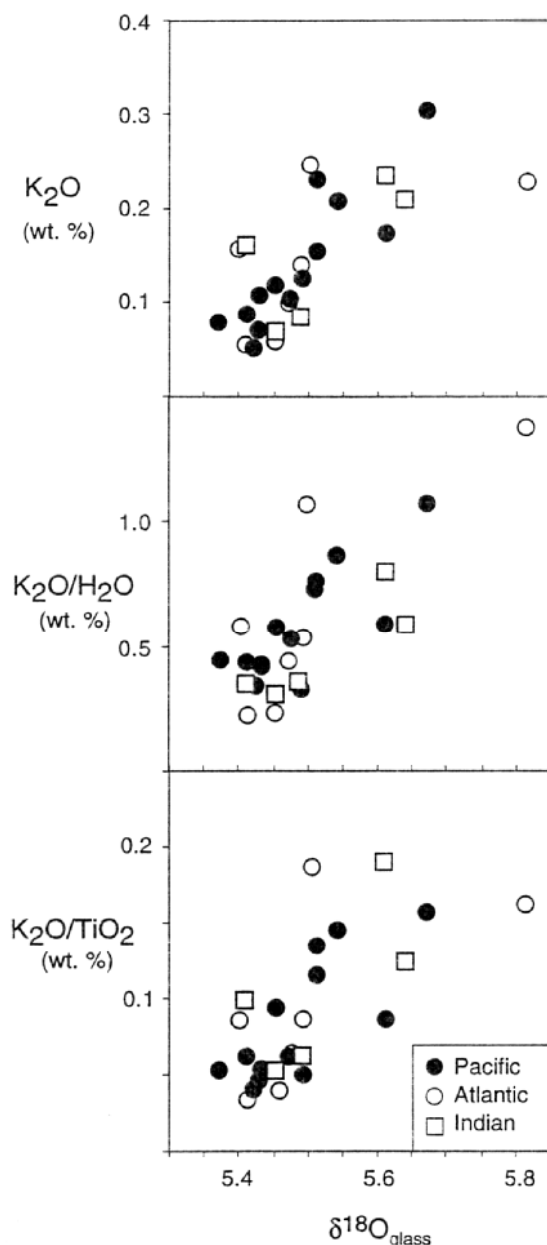


**Figure 9.** Oxygen isotope compositions of nominally fresh MORB glasses and whole-rocks. Unfilled boxes are data collected using conventional (resistance heated) fluorination methods between 1966 and 1993; filled boxes are data collected only on glass using laser-based methods. Where these two data types overlap, conventional fluorination data are shown as white-outlined boxes. Data sources: Taylor (1968), Muehlenbachs and Clayton (1972), Pineau et al. (1976), Kyser et al. (1982), Muehlenbachs and Byerly (1982), Ito et al. (1987), Barrat et al. (1993), Harmon and Hoefs (1995) and references therein, Eiler et al. (2000b), and Eiler and Kitchen (unpublished data).

range extends to values of 5.2 to 5.3 ‰ when three exotic samples from their more recent work on the mid-Atlantic ridge are included), that they have a slightly lower average value than suggested by previous work (5.5 vs. ~5.7 ‰) and, most importantly, that their  $\delta^{18}\text{O}$  values correlate with abundances and abundance ratios of various

5.9 ‰. No systematic correlations were found between  $\delta^{18}\text{O}$  and other geochemical indices thought significant for mantle processes and no statistically significant differences were found between major geographic and compositional groups (e.g. E-MORB vs. N-MORB; Pacific vs. Atlantic). A simple interpretation of these results is that the upper mantle varies little in  $\delta^{18}\text{O}$  and that any variations that do exist are unrelated to other geochemical properties. Nevertheless, Ito et al. emphasized that MORBs vary in  $\delta^{18}\text{O}$  by more than analytical precision and thus it is possible that isotopic ‘signals’ exist that simply were not successfully resolved by their study.

Eiler et al. (2000b) examined oxygen isotope variations of nominally fresh mid-ocean-ridge glasses using laser-based methods. The suite they examined included 28 approximately normal (‘N-’) MORBs distributed evenly among the Pacific, Atlantic and Indian ocean basins; these data are shown as black boxes in Figure 9. This work was recently followed by a study of 51 samples from a portion of the mid-Atlantic ridge, also analyzed in the Caltech lab; these data are unpublished but included as black boxes in Figure 9 for the purposes of completeness. Eiler et al.’s (2000b) study found that NMORBs vary in  $\delta^{18}\text{O}$  by less than suggested by previous studies (5.4 to 5.8 ‰—this



**Figure 10.** Comparison of  $\delta^{18}\text{O}$  values with various minor-element abundances and abundance ratios in NMORBs; data from Eiler et al. (2000b). Lavas from all three major ocean basins (Pacific, Atlantic and Indian) define common trends of increasing  $\delta^{18}\text{O}$  with increasing concentrations of K (and other incompatible elements) and increasing ratios of K abundance to other incompatible element abundances. Model calculations detailed in Eiler et al. (2000b) indicate that these trends are consistent with mixing between low- $\delta^{18}\text{O}$  depleted peridotite and high- $\delta^{18}\text{O}$ , subducted upper oceanic crust. These are the same data shown as gray fields in Figures 4 and 5; their range in  $\delta^{18}\text{O}$  is too great to be accounted for by known fractionations during partial melting and crystallization-differentiation given their relatively small ranges in major element chemistry.

incompatible minor and trace elements (including but not restricted to  $\text{K}_2\text{O}$ ;  $\text{K}_2\text{O}/\text{H}_2\text{O}$  and  $\text{K}_2\text{O}/\text{TiO}_2$ ; Fig. 10). The data in Figure 10 are inconsistent with models in which oxygen isotope variations reflect only fractional crystallization or variations in degree of partial melting of an isotopically homogenous source (these are the data shown as a gray fields in Figs. 4 and 5) but agree with models in which the upper mantle consists of  $\sim 98\%$  depleted peridotite with a  $\delta^{18}\text{O}$  of 5.4 ‰ and variable amounts ( $\sim 2\%$ , on average) of recycled upper oceanic crust and sediments with a bulk  $\delta^{18}\text{O}$  of  $\sim 10\%$  (see Eiler et al. 2000b for details of this model). Similarities among the three major ocean basins in Figure 10 suggest that if recycled crustal components are responsible for differences in  $\delta^{18}\text{O}$  among fresh NMORBs, then they are present in a roughly equal range of abundances in the mantle beneath all three major ocean basins. This interpretation reinforces previous conclusions based on the coupled Pb–Os isotope systematics of NMORBs (Schiano et al. 1997) but runs contrary to common inferences that the sources of NMORBs are a depleted residue of prior melting with little or no back-mixing of recycled crust (see review of Hofmann 1997). This interpretation also suggests that

enrichments in  $^{18}\text{O}$  are different in character from at least some causes of radiogenic-isotope 'enrichment,' which have strong regional variations. For example, Indian ocean MORB's are systematically higher in  $^{87}\text{Sr}/^{86}\text{Sr}$  than Pacific and Atlantic MORBs but conform to the same trends as other MORBs in Figure 10. Finally, these data, whatever their ultimate explanation, require that one make subjective decisions when defining the  $\delta^{18}\text{O}$  of the upper mantle (e.g. should one use the average MORB value, the minimum MORB value, or the  $\delta^{18}\text{O}$  of MORBs at some specific concentration of minor elements?). The differences between these choices are subtle but analytically resolvable and could influence interpretation of oxygen isotope variations in other tectonic settings where 'signals' of exotic components might be superimposed on a template of upper-mantle variability. Collectively, these results suggest one should treat oxygen isotopes as one does other geochemical properties that vary systematically in MORBs (e.g. Nd and Pb isotopes), namely by allowing that the upper mantle in any given region can differ from the global average by  $\sim 0.1$  to  $0.2$  per mil.

### OCEANIC INTRAPLATE BASALTS

Ocean-island basalts (OIB's) provide perhaps the most diverse record of chemical and isotopic variability in the mantle (Hofmann 1997), reflecting, in part, the presence in their mantle sources of constituents that are absent or present in smaller abundances in the upper mantle sources of MORBs. Plausible causes of geochemical diversity in the sources of OIBs include recycled oceanic crust and sediments (Hofmann and White 1982), delaminated continental lithosphere (McKenzie and O'Nions 1983), and relatively primitive or metasomatically enriched rocks that have always resided in the non-lithospheric mantle (DePaolo and Wasserburg 1976). As outlined above, oxygen isotopes can potentially trace subducted material in the mantle sources of basalts and therefore can help discriminate among these sources of geochemical variations among OIBs. Furthermore, there is growing evidence that major-element variations of OIBs constrain the mineralogy and extents and conditions of melting of the sources of ocean-island volcanoes (Elliott et al. 1991; Hauri 1996); oxygen provides an isotopic tracer that is also a major element and therefore could be particularly useful in testing and advancing such studies. Other classes of oceanic intraplate basalts—e.g. oceanic plateaus; off-axis and isolated seamounts—have not been examined in any detail for their oxygen isotope geochemistry and will not be discussed here (although they are an attractive target for future studies).

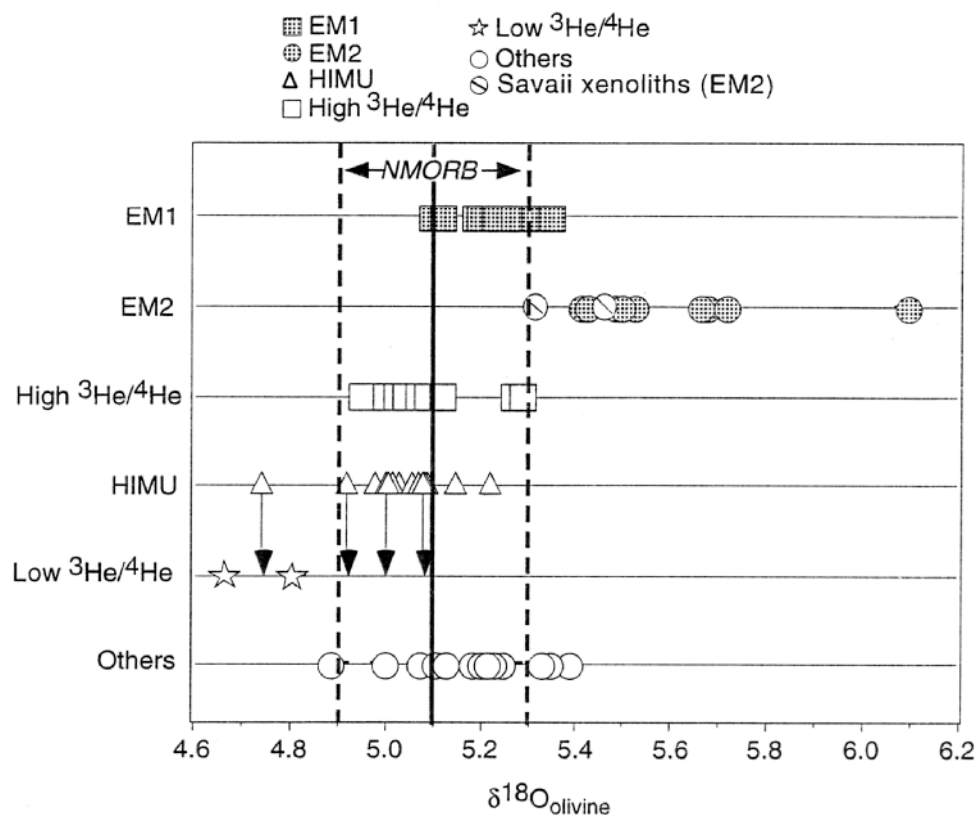
Many studies have characterized the oxygen isotope ratios of ocean island basalts using conventional whole-rock analyses. The most comprehensive of these studies is the review paper of Harmon and Hoefs (1995), which concludes that, after filtering the data base to remove differentiated and altered rocks, approximately half of all OIBs have  $\delta^{18}\text{O}$  values outside the range of fresh MORBs and that the average value for OIBs is  $^{18}\text{O}$  depleted compared to MORBs. These authors suggest that low  $\delta^{18}\text{O}$  values of OIBs are particularly associated with 'HIMU'-type radiogenic isotope signatures (the most distinctive property of which is high  $^{206}\text{Pb}/^{204}\text{Pb}$ ; Zindler and Hart 1986) and are caused by high concentrations of recycled lower oceanic crust in their mantle sources. They also note that the two volcanic centers that are the sources of most known low- $\delta^{18}\text{O}$  OIB's (Hawaii and Iceland) are also locations that erupt basalts with unusually high  $^3\text{He}/^4\text{He}$  ratios and thus low  $\delta^{18}\text{O}$  values might also be a property of un-degassed lower mantle. Finally, subducted sediment is called on as the cause of high  $\delta^{18}\text{O}$  values in some 'enriched' OIBs, principally based on the results of Woodhead et al. (1993) who found an increase in  $\delta^{18}\text{O}$  with decreasing  $^{143}\text{Nd}/^{144}\text{Nd}$  among glasses from the Pitcairn seamounts. However, oxygen isotope variations among OIB whole-rocks and glasses are ambiguous both because there is substantial overlap between  $\delta^{18}\text{O}$  values of OIBs

having very different radiogenic isotope compositions and because (with the exception of the Pitcairn seamounts)  $\delta^{18}\text{O}$  generally does not correlate well with other geochemical properties within suites of related lavas.

Oxygen isotope ratios of ocean-island basalts have been re-examined using laser-based techniques in detailed studies of Hawaiian and Icelandic lavas (both aimed at establishing the origin of  $^{18}\text{O}$ -depleted compositions in some OIBs) (Eiler et al. 1996a,b), the Canary islands (Thirlwall et al. 1997) and Tristan da Cunha/Gough (Harris et al. 2000), and one survey of approximately 60 globally-distributed OIBs (Eiler et al. 1996a); these data are summarized in the following sections:

### Survey of ocean islands

This discussion is organized by sub-dividing samples into groups that easily fit end-member categories previously defined by radiogenic isotope systematics (Zindler and Hart 1986); ‘low- $^3\text{He}/^4\text{He}$ ’ lavas discussed in Eiler et al. (1996a) are excluded from this discussion and are instead mentioned below in the context of work on Hawaiian and Icelandic lavas. Figure 11 summarizes the data discussed in the following paragraphs.



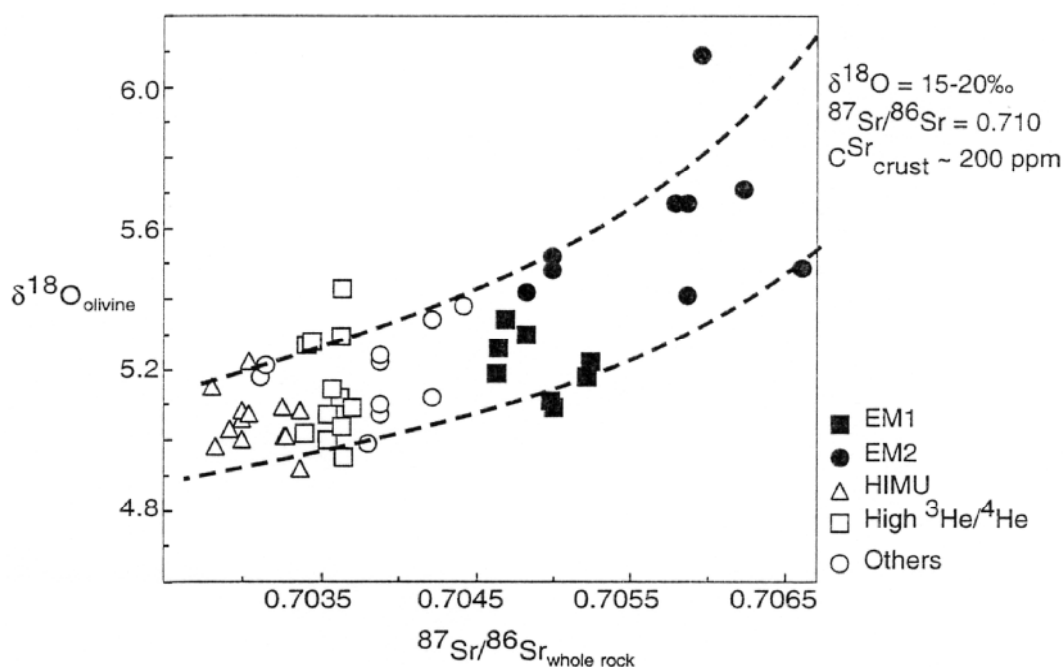
**Figure 11.** Oxygen isotope compositions of olivines in ocean island basalts, organized by geochemical sub-type as defined by radiogenic isotope compositions (Zindler 1986; see text for details). The vertical band between heavy dashed lines marks the range in  $\delta^{18}\text{O}$  of olivine in equilibrium with NMORBs (assuming a melt-olivine fractionation of 0.5 ‰); the lower- $\delta^{18}\text{O}$  half of this range is typical of incompatible-element poor MORBs and the upper- $\delta^{18}\text{O}$  half is typical of incompatible-element rich MORBs (see Fig. 10). The ‘low- $^3\text{He}/^4\text{He}$ ’ category refers to lavas with  $^3\text{He}/^4\text{He}$  ratios lower than 8 Ra; this is a characteristic often associated with  $^{18}\text{O}$ -depleted compositions (regardless of other radiogenic-isotope properties) and is discussed in the text in reference to Hawaiian and Icelandic lavas. Arrows indicate samples that arguably belong to more than one group. These data are taken from Eiler et al. (1996a).

**EM1.** ‘EM1’-type ocean-island lavas are most simply characterized by strongly sub-chondritic (‘enriched’)  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios but  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios within the range of or only slightly higher than estimates for bulk Earth (Zindler and Hart 1986). These characteristics have been attributed to subducted pelagic sediments in their mantle sources (perhaps with a component of subducted oceanic basalt; Zindler and Hart 1986; Weaver 1991; Woodhead et al. 1993), although Sun and McDonough (1989) argued that the trace-element abundances of EM1 lavas are more consistent with intra-mantle metasomatic or magmatic differentiation. Woodhead et al. (1993) present oxygen isotope data for submarine glasses from the Pitcairn seamounts (perhaps the most well characterized, end member ‘EM1’ hotspot), which document correlations between  $\delta^{18}\text{O}$  and various radiogenic isotope ratios and suggest that their mantle sources contain up to 10 % recycled sediment. However, the most extreme radiogenic isotope compositions in the Pitcairn seamounts are found in relatively evolved lavas, raising the question of whether they are  $^{18}\text{O}$ -rich because of the composition of their sources or because of their extent of magmatic evolution. Subsequent examination of olivine and plagioclase phenocrysts in basalts from nearby Pitcairn island, where the most extreme radiogenic isotope compositions are found in relatively magnesian basalts, found no evidence for  $\delta^{18}\text{O}$  values outside the range for MORBs (Eiler et al. 1995). These data demonstrate that the enriched radiogenic isotope signature of EM1 can exist in the mantle sources of OIBs without any deviations in oxygen isotope ratio from typical upper mantle values, and thus that this end member is likely produced by little ( $< \sim 1$  %) or no recycled crust. This conclusion is consistent with oxygen isotope compositions of less extreme EM1-type ocean island lavas from Kerguelan and Heard island (Eiler et al. 1996a).

**EM2.** ‘EM2’ type ocean island basalts are characterized by  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios that are greater than (more ‘enriched’ than) that estimated for bulk earth but a  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio that is near or slightly above (more ‘depleted’ than) chondritic (Zindler and Hart 1986). The compositions of EM2-type OIB has been widely ascribed to the presence of subducted sediments in their mantle sources (White and Hofmann 1982; Zindler and Hart 1986; Hofmann 1997); they arguably present the least controversial case for recycled crust in the sources of OIBs. Nine near-end-member ‘EM2’ lavas from the Society islands and Samoa (as well as two related Samoan xenoliths) were included in Eiler et al.’s (1996a) survey. Olivine in these lavas is consistently  $^{18}\text{O}$ -enriched relative to typical terrestrial basalts, averaging  $5.6 \pm 0.2$  ‰ and having almost no overlap in  $\delta^{18}\text{O}$  with MORBs and most other OIB’s (Fig. 11). The only other oceanic basalts to have such consistently high  $\delta^{18}\text{O}$  values are OIB from Koolau, Hawaii, and certain arc-related basalts having distinctive chemistries suggesting high degrees of melting; both of these are detailed below. The association of  $^{18}\text{O}$ -enrichment with high  $^{87}\text{Sr}/^{86}\text{Sr}$  is further emphasized in Figure 12, which compares the  $\delta^{18}\text{O}$  values of olivines to the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios measured on host whole rocks for representative OIBs from Eiler et al.’s (1996a) survey; curves illustrating the expected trends for mixing recycled sediment with depleted mantle are shown for comparison (this calculation is a minor modification of that detailed in Eiler et al. 1996, changed to reflect new constraints on the  $\delta^{18}\text{O}$  of MORBs; Fig. 9).

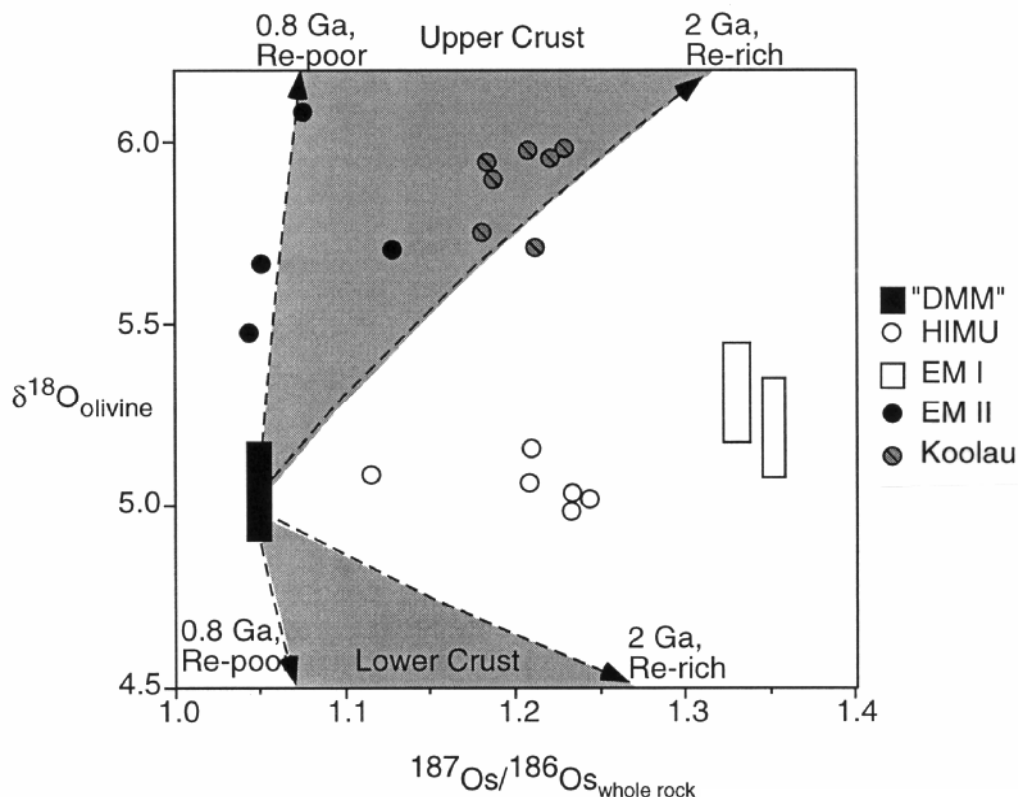
**HIMU.** The ‘HIMU’ radiogenic isotope signature is most distinctive for its high  $^{206}\text{Pb}/^{204}\text{Pb}$  ratio, which is frequently explained as a consequence of sampling large mass fractions (10’s of %) of  $\sim 1$  to 2 Ga recycled oceanic crust (e.g. Hauri and Hart 1993). Sun and McDonough (1989) instead suggest that distinctive trace-element concentrations of HIMU lavas are better explained by processes of magmatic and/or metasomatic differentiation within the mantle; a similar proposal was put forward by





**Figure 12.** Comparison of  $\delta^{18}\text{O}$  values with  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in representative ocean-island basalts, organized by sub-type as defined by radiogenic isotope systematics (see Fig. 11; data from Eiler et al. 1996a). Low- $^3\text{He}/^4\text{He}$  lavas are a special case discussed in Eiler et al. (1996a) and in the text of this chapter and are excluded here. The heavy dashed curves mark the range of mixing hyperbolae between depleted mantle (based on data for NMORBs; Figs. 9 and 10) and high- $\delta^{18}\text{O}$  siliciclastic sediments.

Halliday et al. (1990) based on  $^{207}\text{Pb}$ - $^{206}\text{Pb}$ - $^{204}\text{Pb}$  systematics. Eiler et al. (1996a) measured the  $\delta^{18}\text{O}$  of olivine phenocrysts from 14 near-end-member HIMU basalts ( $^{206}\text{Pb}/^{204}\text{Pb}$  from 20.0 to 21.8) and found them to be, with one exception, the most homogenous independently defined group of OIB (10 span a range of only 0.11 ‰). They are also the only group to have an average  $\delta^{18}\text{O}$  that is statistically indistinguishable from that of the ‘depleted’ (low  $\delta^{18}\text{O}$ , incompatible-element-poor) end of the range for NMORBs; Fig. 10). At face value, this result is difficult to reconcile with models in which the mantle sources of HIMU lavas contain large mass fractions of recycled seafloor basalt: One might argue that the  $^{18}\text{O}$ -rich and  $^{18}\text{O}$ -poor parts of the oceanic crust simply balance to have no contrast in  $\delta^{18}\text{O}$  with upper mantle peridotites, but this explanation requires an implausibly delicate balance of the abundances of two materials that differ strongly in  $\delta^{18}\text{O}$  from each other and from the upper mantle. This point is emphasized further in Figure 13, which plots  $\delta^{18}\text{O}$  vs.  $^{187}\text{Os}/^{186}\text{Os}$  for the subset of OIBs from Eiler et al.’s (1996a) survey that were also characterized for Os isotope composition and compares the data to calculated mixing trends between depleted upper mantle (based on data for NMORBs; Fig. 10) and either upper or lower oceanic crust (this calculation assumes a model for Os abundances and isotope ratios in the end members given by Hauri and Hart 1993). In this figure, ‘EM2’ (and certain ‘enriched’ lavas from Hawaii also shown for comparison) are consistent with derivation from sources rich in recycled upper oceanic crust, but ‘HIMU’ and ‘EM1’ lavas are not derived from sources rich in recycled crust, barring fortuitous mixtures of upper and lower crust as mentioned above. On this basis alone, one would conclude that HIMU and EM1 isotopic signatures are a consequence of intra-mantle metasomatic enrichments or trace components of subducted materials.



**Figure 13.** Comparison of  $\delta^{18}\text{O}$  values with  $^{187}\text{Os}/^{186}\text{Os}$  ratios in representative ocean-island basalts, organized by sub-type as defined by radiogenic isotope systematics (see Fig. 11; data from Eiler et al. 1996a, Hauri and Hart 1993, Reisberg et al. 1993, Lassiter and Hauri 1997, and Hauri, unpublished data). Fields for 'EM1' lavas are based on comparisons of  $\delta^{18}\text{O}$  values and  $^{187}\text{Os}/^{186}\text{Os}$  ratios from closely related samples. Samples from Koolau, Hawaii, are shown for comparison. Dashed curves bounding gray fields mark the range of mixing hyperbola between depleted mantle (based on data for NMORBs; Figs. 9 and 10) and either high- $\delta^{18}\text{O}$  oceanic crust (i.e. altered basalt) or low- $\delta^{18}\text{O}$  oceanic crust (i.e. hydrothermally altered layer 3 gabbros). Re/Os ratios and Os isotope compositions are taken from models of crustal recycling presented in Hauri and Hart (1993).

### High $^3\text{He}/^4\text{He}$

One of the more longstanding conjectures about the oxygen isotope geochemistry of the mantle is that lower-mantle reservoirs rich in primitive noble gases are  $^{18}\text{O}$  depleted compared to the upper mantle. This idea was originally based on the observations that low- $\delta^{18}\text{O}$  basalts are common in Hawaii and Iceland (Kyser et al. 1982; Kyser 1986; Harmon and Hoefs 1995)—locations that erupt basalts with unusually high  $^3\text{He}/^4\text{He}$  ratios, which are in turn interpreted as an indication that their mantle sources contain relatively un-degassed materials, perhaps from the lower mantle (Kurz 1991). Oxygen isotope compositions of olivine phenocrysts have been measured for 21 lavas from Loihi, Kauai, and the Juan Fernandez islands having  $^3\text{He}/^4\text{He}$  ratios of 15 Ra or greater (Fig. 11; see also Eiler et al. 1996b)—a range that is unambiguously distinct from MORB and most other ocean-island basalts. Olivines from these lavas vary little in  $\delta^{18}\text{O}$  and have an average value that is indistinguishable from those in most basalts from other tectonic settings or from olivine in upper-mantle xenoliths. Although these results may simply reflect decoupling of volatiles from their long-term mantle sources (for instance, by intra-mantle metasomatism), they certainly provide no positive evidence that mantle reservoirs having high  $^3\text{He}/^4\text{He}$  ratios differ in  $\delta^{18}\text{O}$  from typical upper mantle rocks.

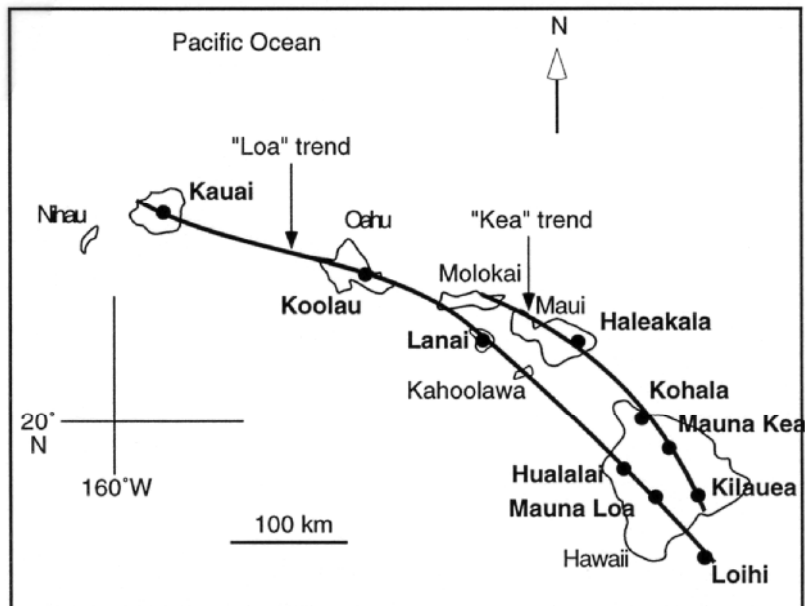
Thirlwall et al. (1999), and McPherson et al. (2000) recently defended the hypothesis of  $^{18}\text{O}$  depletion in high  $^3\text{He}/^4\text{He}$  reservoirs based on studies of basalts from the Reykjanes ridge and Manus basin, respectively. The evidence in these studies is suggestive but not easily reconciled with the observations that lavas with strongly elevated  $^3\text{He}/^4\text{He}$  ratios are 'normal' in  $\delta^{18}\text{O}$  (Fig. 11). Nevertheless, the question of vertical stratification of  $\delta^{18}\text{O}$  in the earth's mantle is an important one and will doubtless continue to be the focus of new work and diverse interpretations.

### Detailed studies

The preceding paragraphs describe general patterns in the oxygen isotope geochemistry of oceanic-island lavas, but conclusions based on broad overviews of this type can be superficial without also considering detailed studies of individual volcanic centers. In the following paragraphs I summarize the results of recent work on the three oceanic-island volcanic centers that have been studied in detail: Hawaii, Iceland, and the Canary islands. All three of these sets of studies share a focus on exploration of  $^{18}\text{O}$ -depleted compositions in oceanic islands (but differ in various other important details).

**Hawaii.** It has been recognized for nearly 20 years that Hawaiian lavas are  $^{18}\text{O}$ -depleted compared to MORBs and most terrestrial and lunar basalts generally (Kyser et al. 1982). Given the importance of the Hawaiian islands to studies of ocean-island volcanism, this anomaly has been the subject of several detailed studies (e.g. Garcia et al. 1989), but until recently remained enigmatic because of the lack of obvious relationships between  $\delta^{18}\text{O}$  and other geologic and geochemical properties. A series of laser-fluorination studies of phenocrysts and glasses (Eiler et al. 1996b; Eiler et al. 1996c; Wang and Eiler 2000) revealed several such relationships, although their significance remains debated; the most important of these are: (1) Among sub-aerial, shield building lavas, low- $\delta^{18}\text{O}$  compositions are restricted to 'Kea trend' volcanoes (Kilauea, Mauna Kea, Kohala, and Haleakala; Fig. 14); (2) Koolau and Lanai (Fig. 14) are characterized by high  $\delta^{18}\text{O}$  values, comparable to those in 'EM2' lavas (Figs. 11 to 13 above; Koolau lavas are included in Fig. 13); and (3)  $\delta^{18}\text{O}$  correlates with various radiogenic isotope ratios, although these correlations are dominated by differences between volcanoes rather than trends exhibited by lavas from any one volcano; see Eiler et al. (1996b) for details of these correlations. Eiler et al. (1996b) proposed that  $^{18}\text{O}$ -enriched compositions in Koolau and Lanai lavas reflect a component of recycled upper-crustal rocks and/or sediments in their mantle sources, in agreement with previous suggestions that such components can explain 'enriched' trace-element and radiogenic-isotope compositions of these lavas (Roden et al. 1994). This interpretation has been followed by more recent papers adding Os isotope constraints (Hauri 1996; Lassiter and Hauri 1996), but argued against on the basis of some of the same data (Bennett et al. 1996).

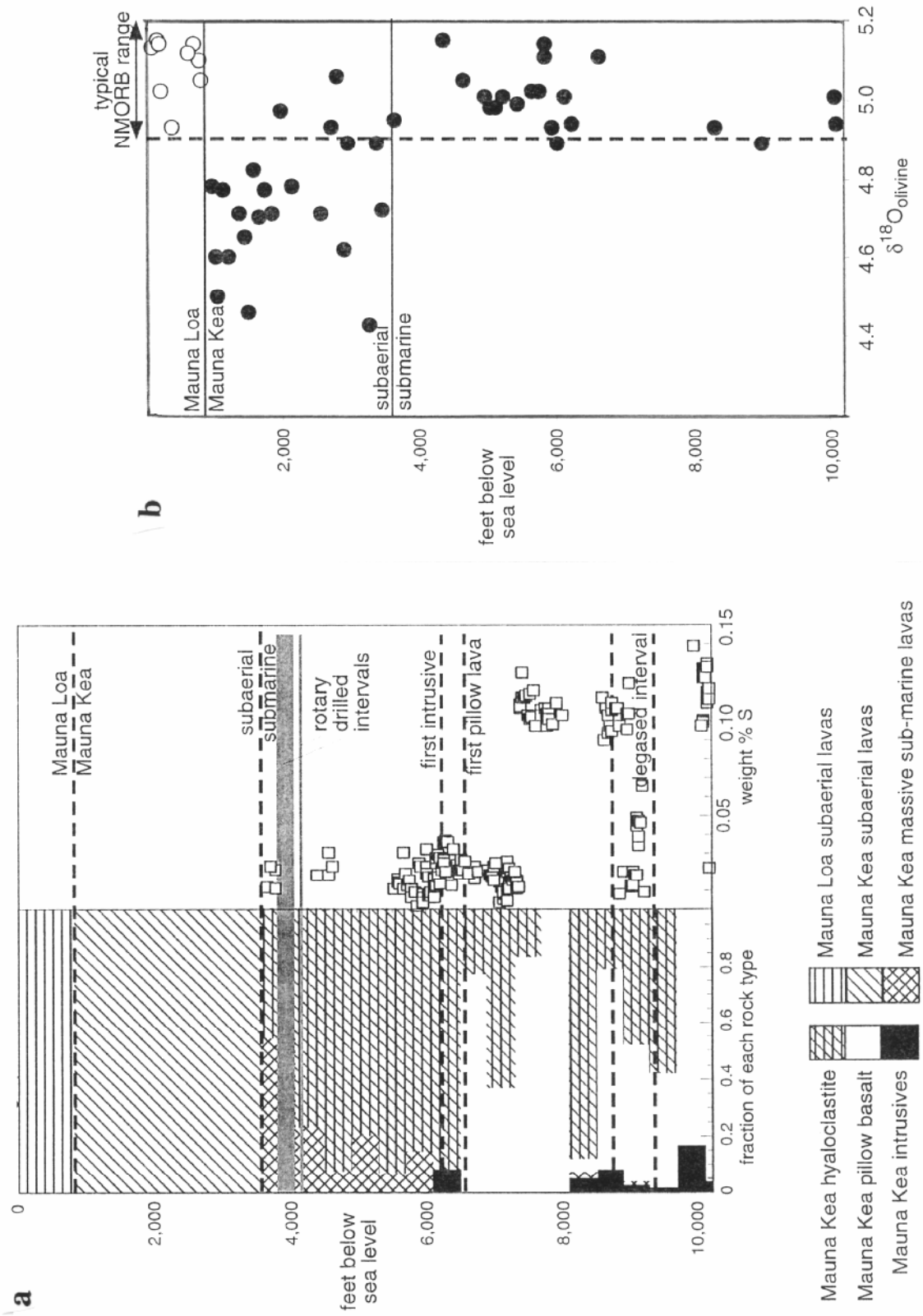
The origin of  $^{18}\text{O}$ -depleted compositions has been more hotly debated and remains more ambiguous: Eiler et al. (1996b) noted similarities between radiogenic isotope compositions of low- $\delta^{18}\text{O}$ , Kea trend lavas on one hand and modern MORBs on the other (e.g. decreasing  $\delta^{18}\text{O}$  is associated with decreasing  $^3\text{He}/^4\text{He}$ ) and concluded that  $^{18}\text{O}$ -depleted compositions are a consequence of contamination by layer-3 gabbros in the Pacific plate. Lassiter and Hauri (1998) instead suggested that  $^{18}\text{O}$ -depleted compositions sample recycled hydrothermally altered, ultramafic portions of oceanic lithosphere entrained in the Hawaiian 'plume.' However, both of these interpretations are inconsistent with the most recent data from Wang and Eiler (2000) which show that the  $^{18}\text{O}$ -depleted character of Mauna Kea lavas goes away sharply at the submarine-to-subaerial transition traversed by the Hawaiian Scientific Drilling Project ('HSDP'; Fig. 15) without the accompanying change in radiogenic isotope compositions one would

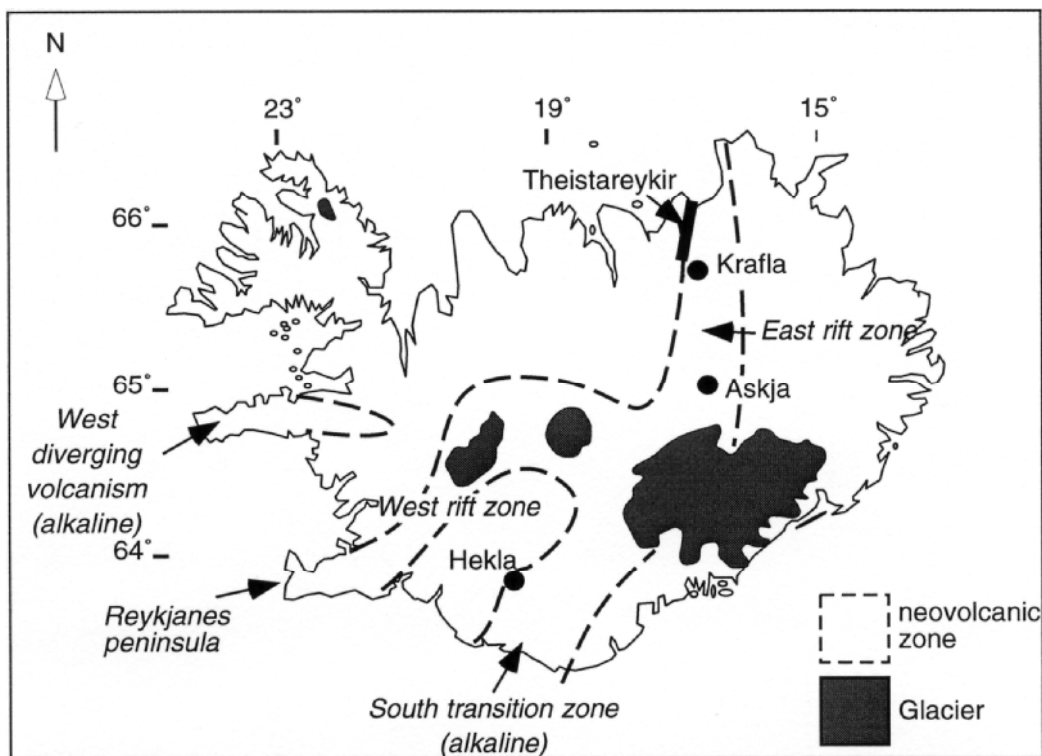


**Figure 14.** Map of the Hawaiian Islands. Volcanoes whose oxygen isotope geochemistry has been examined are marked with filled circles and labeled in bold. The 'Loa' and 'Kea' trends of volcanoes are indicated with solid curves; lavas from these two trends are distinct from one another in several geochemical properties (i.e. radiogenic isotope ratios) and also differ systematically in oxygen isotope composition: 'Loa' trend volcanoes are generally similar in  $\delta^{18}\text{O}$  to MORBs and other ocean island lavas and include two edifices (Koolau and Lanai) with high  $\delta^{18}\text{O}$  lavas; 'Kea' trend volcanoes have abundant low- $\delta^{18}\text{O}$  lavas.

predict from either the Eiler et al. or Lassiter and Hauri hypotheses. Wang and Eiler (2000) suggest that  $^{18}\text{O}$ -depleted compositions in Kea-trend Hawaiian volcanoes are instead a product of contamination by hydrothermally altered rocks in rift zones in the volcanic edifice (analogous to processes inferred from study of Puu Oo lavas in Kilauea's east rift zone; Garcia et al. 1997). This hypothesis explains the lack of  $^{18}\text{O}$ -depleted lavas in the 'Loa trend' volcanoes because of the low supply of meteoric water to their rift zones (such that hydrothermally altered crustal rocks are less abundant) and

**Figure 15 (opposite page).** (a) Stratigraphic profile of the core recovered from the 2nd phase of the Hawaiian Scientific Drilling Project (HSDP). Relative abundances of rock types are indicated in the left panel using symbols described in the key; sulfur concentrations in glass (a measure of extent of degassing) are shown in the right panel; major boundaries in volcanic evolution and degassing history are indicated by heavy dashed lines. This figure is taken from Stolper, Depaolo and Thomas' (2000) description of the HSDP core. (b) Profile of oxygen isotope compositions of olivines from the HSDP core. The vertical field defined by the dashed line marks the range in  $\delta^{18}\text{O}$  typical of upper-mantle basalts (based on data for MORBs and an assumed melt-olivine fractionation of 0.5 per mil). Values of  $\delta^{18}\text{O}$  for Mauna Loa lavas (unfilled circles) are typical of those for lavas from other Loa trend volcanoes (excepting Koolau and Lanai, which are higher in  $\delta^{18}\text{O}$ ). Low values of  $\delta^{18}\text{O}$  at the top of the Mauna Kea section of the core are typical of subaerial lavas from other Kea trend volcanoes, including recent lavas from the Puu Oo east rift zone (Garcia et al. 1998). The 'subaerial to submarine' transition marks the boundary between Mauna Kea lavas erupted above sea level and underlying Mauna Kea lavas erupted underwater (identified based on vascularity and other petrographic criteria). Below this boundary, Mauna Kea lavas are indistinguishable in  $\delta^{18}\text{O}$  from most Loa-trend lavas and typical terrestrial basalts generally. No such discontinuity exists at this boundary in other source-related geochemical properties (i.e. radiogenic isotope ratios).



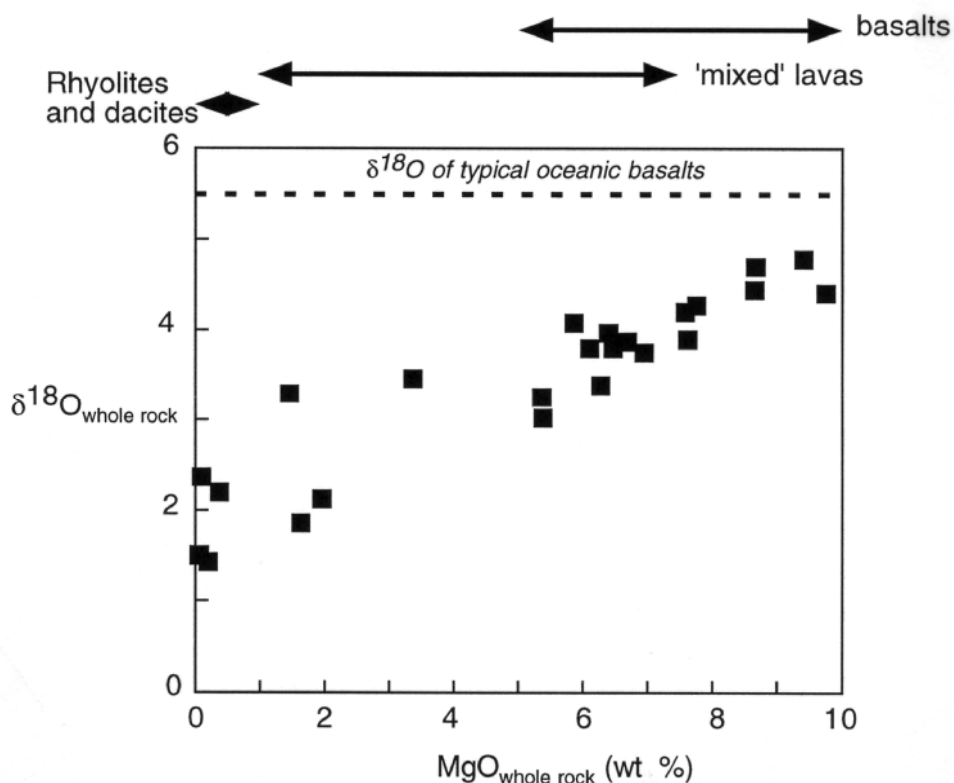


**Figure 16.** Map of Iceland, emphasizing major volcanic features. The dashed curves outline neovolcanic provinces that have been active since the last glacial maximum. Central volcanic complexes (characterized by abundant evolved magmas) are marked as filled circles and labeled. Theistareykir is a segment of the northern neovolcanic province; data for post-glacial lavas from here are shown in Figure 19. Large glaciers are marked in gray.

the absence of low- $\delta^{18}\text{O}$  values in submarine lavas because of the presumed isolation of their vents from low-pressure meteoric-hydrothermal systems that promote generation of  $^{18}\text{O}$ -depleted rocks. These samples are still being characterized for other geochemical properties and thus detailed tests of this or other explanations of the data in Figure 15 have yet to be performed.

**Iceland.** Iceland is a section of the mid-Atlantic ridge that is anomalous for its unusually thick crust and the ‘enriched’ compositions of its lavas compared to adjacent sections of the mid ocean ridge; these features are widely attributed to a focused mantle upwelling or ‘plume’ in the sub-Icelandic mantle (e.g. Schilling et al. 1982; see Fig. 16). Iceland is arguably similar in importance to Hawaii in the general study of ocean-island volcanism because of its excellent exposure, close relationship to a seafloor spreading center, and the unusually high  $^3\text{He}/^4\text{He}$  ratios of some of its lavas (Condomines et al. 1983; Poreda et al. 1986).

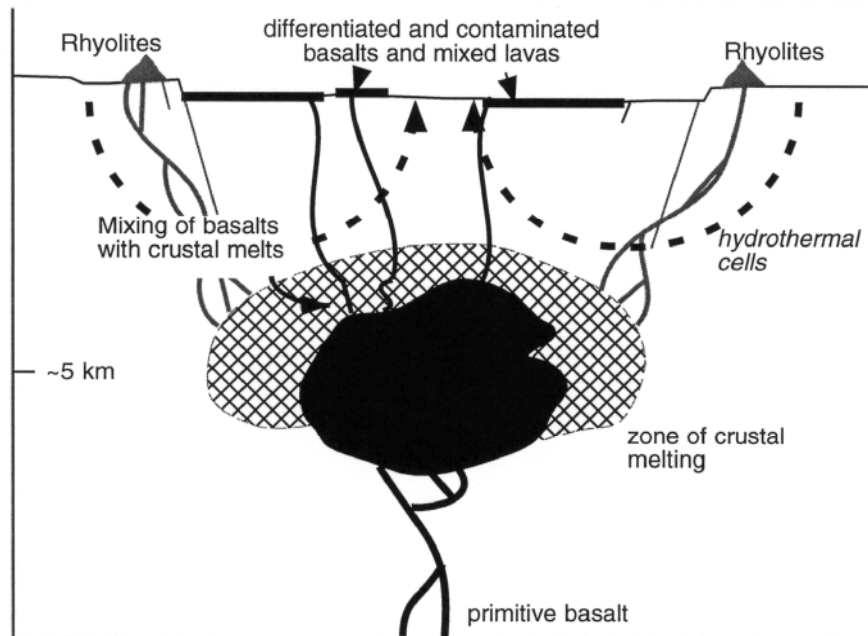
Iceland sits at high latitudes and, therefore, receives strongly  $^{18}\text{O}$ -depleted precipitation. In addition, it is undergoing high rates of extension and volcanism, promoting deep-seated meteoric-hydrothermal systems in the crust (Bjornsson 1985). As a result, Iceland has a greater contrast in  $\delta^{18}\text{O}$  between the crust and mantle than any other well-studied oceanic volcanic center (Gautason and Muehlenbachs 1998). Because the oxygen isotope ‘signals’ of crustal contamination are so strong there, conventional studies of whole-rock specimens are adequate for producing clear records of relationships between  $\delta^{18}\text{O}$  and other geochemical properties among highly evolved and contaminated rocks (andesites, dacites and rhyolites). There have been many such studies conducted on a variety of scales (i.e. single eruptive centers vs. surveys of all of Iceland); a particularly



**Figure 17.** Comparison of  $\delta^{18}\text{O}$  values with MgO concentrations in whole-rock samples from Krafla, a central volcano complex in Iceland's northern neovolcanic zone; data from Nicholson et al. (1991). MgO-poor, low- $\delta^{18}\text{O}$  rhyolites and dacites are interpreted as melts of hydrothermally altered crustal rocks; mixing between these melts and basalts generates the trend of decreasing  $\delta^{18}\text{O}$  with decreasing MgO. It is not clear from studies of such highly evolved suites whether subtle differences in  $\delta^{18}\text{O}$  between the most magnesian lavas (MgO of between 8 and 9 wt %) and typical terrestrial basalts are caused by subtle crustal contamination or are instead a property of the sub-Icelandic mantle.

detailed and revealing example is the work of Nicholson et al. (1991), who documented the relationship between indices of increasing differentiation (e.g. decreasing MgO) and increasing extent of contamination by hydrothermally altered crustal rocks or their melts (as monitored by decreasing  $\delta^{18}\text{O}$ ); these data are reproduced in Figure 17 and a cartoon illustrating a common model for such contamination processes is shown in Figure 18. Other studies establish that low  $\delta^{18}\text{O}$  Icelandic lavas are characterized by low  $^3\text{He}/^4\text{He}$  ratios (Condomines et al. 1983)—re-enforcing similar results from Hawaii, described above, and the finding that low  $\delta^{18}\text{O}$  values in other OIB volcanic centers are also associated with low  $^3\text{He}/^4\text{He}$  (Eiler et al. 1996a). Low  $^3\text{He}/^4\text{He}$  ratios are characteristic of even relatively young crustal rocks and thus this signature is consistent with pollution of basalts by  $^{18}\text{O}$ -depleted crust.

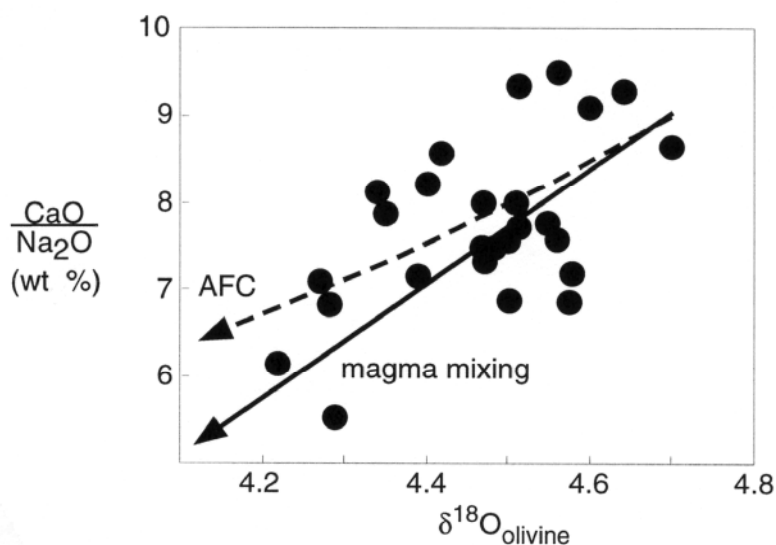
The oxygen isotope geochemistry of relatively primitive Icelandic lavas is more controversial. There is abundant evidence that basalts and basaltic andesites from this setting are often (although not ubiquitously)  $^{18}\text{O}$ -depleted compared to MORBs (Hemond et al. 1993), but there is no consensus as to whether this is because most such lavas have undergone small amounts of crustal contamination known to produce profound  $^{18}\text{O}$ -depletions in more evolved lavas or instead because the mantle beneath Iceland contains one or more  $^{18}\text{O}$ -depleted components. It is this author's prejudice that



**Figure 18.** Schematic illustration of models for the contamination of Icelandic basalt in crustal hydrothermal / magmatic systems. Mafic magma is shown in black; the hatched area marks the region of the crust adjacent magma chambers where hydrothermally altered rocks are partially melted. Rhyolites (presumed erupted crustal melts) are shown in gray. Mafic magmas are presumed to mix with siliceous melts while passing through the zone of partially melted crustal rocks. Dashed arrows schematically indicate flow of water through the crust. Adapted from models described by Condomines et al. (1983), Nicholson et al. (1991), Sigmarsson et al. (1992), Hemond et al. (1993), and Jonasson (1994).

the second hypothesis demands a high burden of proof in a system with such extreme  $^{18}\text{O}$  depletion in hydrothermally altered rocks of the pre-existing crust, but both explanations are plausible and worth exploring. Gee et al. (1998) found evidence that both 'depleted' and 'enriched' primitive basalts in the Reykjanes peninsula (Fig. 16) have  $\delta^{18}\text{O}$  values within the range of MORBs, suggesting that the compositional heterogeneity in the sub-Icelandic mantle is not associated with variations in  $\delta^{18}\text{O}$ , but that lavas with intermediate compositions are frequently  $^{18}\text{O}$ -depleted, suggesting that contamination by  $^{18}\text{O}$ -depleted rocks accompanies crustal mixing processes. Similarly, Eiler et al. (2000c) examined oxygen isotope variations in recent lavas from Theistareykir in Iceland's northern neovolcanic zone (Fig. 16) and found subtle, ubiquitous  $^{18}\text{O}$ -depletions relative to MORBs that were interpreted as a consequence of contamination during crustal mixing processes. This study revealed usually simple correlations between  $\delta^{18}\text{O}$  and other chemical indices; Figure 19 illustrates a representative view of these data and various models of crustal contamination that plausibly explain them, calling on assimilation and mixing processes previously suggested to explain the oxygen isotope geochemistry of evolved lavas from Krafla and similar central volcanic complexes (Figs. 17 and 18). Note that the conclusions of this study contrast with interpretations of the major and minor element chemistry of Theistareykir lavas as a consequence of dynamic melting of the Iceland plume (Slater et al. 1998) and are likely to be debated. Finally, Thirlwall et al. (1999) recently reported  $^{18}\text{O}$ -depleted compositions in submarine lavas from the Reykjanes ridge and suggested that they provided evidence for an  $^{18}\text{O}$ -depleted component of the mantle beneath Iceland,





**Figure 19.** Comparison of  $\delta^{18}\text{O}$  values of olivines with  $\text{CaO}/\text{Na}_2\text{O}$  ratios of whole-rocks for recent Theistareykir basalts, northern Iceland (data of Eiler et al. 2000c). The positive correlation is consistent with subtle decreases in  $\delta^{18}\text{O}$  accompanying increases in degree of magmatic differentiation. The observed trend can be modeled as either magma mixing (solid curve, calculated assuming a low- $\delta^{18}\text{O}$  end member similar to Krafla ‘mixed’ lavas; Fig. 17) or as an Assimilation-Fractional-Crystallization process (dashed curve, calculated assuming an assimilant similar in composition to typical Icelandic upper-crustal altered volcanics). Details of both model curves are provided in Eiler et al. (2000c).

perhaps related to entrainment in that mantle of outer core material. This result has yet to be fully explored but will doubtless provide an interesting new insight on the problem of  $^{18}\text{O}$ -depleted oceanic magmas once this is done.

**Canary Islands.** The Canary Islands do not have the prominent role in studies of oceanic intraplate volcanism shared by Hawaii and Iceland but have been the focus of a detailed oxygen isotope study in an effort to understand the origin and evolution of their lavas (Thirlwall et al. 1997). This work revealed relationships among isotopic compositions of Pb, Nd and O consistent with primary Canary Island magmas being relatively low in  $\delta^{18}\text{O}$  (equal to or less than values of NMORBs) and ‘HIMU’-like in their radiogenic isotope signatures, and that magmas were extensively contaminated by high- $\delta^{18}\text{O}$  low- $^{143}\text{Nd}/^{144}\text{Nd}$ , low- $^{206}\text{Pb}/^{204}\text{Pb}$  crustal rocks during their differentiation. Thirlwall et al. favor an interpretation that the primary magmas are significantly  $^{18}\text{O}$ -depleted compared to most upper mantle rocks and, thus, might sample recycled lower oceanic crust; however, they noted that low- $\delta^{18}\text{O}$  lavas are significantly evolved and might have taken on their  $^{18}\text{O}$ -depleted character during contamination by hydrothermally altered rocks in the current lithosphere (i.e. a different contaminant from that suspected to be responsible for the properties of unusually high- $\delta^{18}\text{O}$  lavas).

To summarize, recent research using high-precision laser-based methods suggests that there is no systematic difference in  $\delta^{18}\text{O}$  between the mantle sources of most ocean-island lavas on one hand and MORBs on the other (Fig. 11), but that many ocean-island centers erupt lavas higher and/or lower than the MORB range (Figs. 12 to 19), plausibly reflecting mantle processes in some cases and crustal processes in others. The diversity of ocean island lavas does not support simple generalizations; nevertheless, the weight of evidence suggests that  $^{18}\text{O}$ -enriched compositions in magnesian lavas are most often

explained by high- $\delta^{18}\text{O}$ , enriched mantle components (although  $^{18}\text{O}$  enrichments of comparable magnitude can result from high extents of crystallization-differentiation and crustal contamination; Harris et al. 2000). Anomalously low  $\delta^{18}\text{O}$  values are debated, although the two most extensively studied examples (Hawaii and Iceland) reveal evidence implicating crustal contamination processes. These results suggest that a key to producing  $^{18}\text{O}$ -depleted ocean-island lavas may be contamination of magmas in extensional rift zones that receive sufficient meteoric water to have vigorous hydrothermal systems. This conclusion mirrors that of Taylor and Sheppard 1986, regarding the origin of much more extreme  $^{18}\text{O}$  depletions characteristic of some continental silicic volcanic centers (e.g. Yellowstone; see also Bindeman and Valley 2000) but not others (e.g. central Nevada and San Juan volcanic fields). Nevertheless, it is clear that  $^{18}\text{O}$ -depleted rocks are subducted and occasionally found as high-pressure mantle xenoliths. Therefore we should expect to eventually find evidence for their oxygen isotope signatures in oceanic basalts derived from sources in which these rocks are entrained.

### CONTINENTAL INTRAPLATE BASALTS

Continental intra-plate lavas are good candidates for oxygen isotope studies because of the likelihood that they have been significantly contaminated by  $^{18}\text{O}$ -rich continental crustal rocks (i.e. the 'signals' in the oxygen isotope compositions of such lavas should be strong and well-correlated with important processes in their petrogenesis). This expectation is born out by studies of continental flood basalts based on conventional analyses of whole-rock specimens (e.g. Carlson 1984; Peng et al. 1994; Harmon and Hoefs 1995, and references therein). However, these remain the only major class of terrestrial basalts that have not yet been explored systematically using methods of high-precision laser-fluorination. A recent study of continental flood basalts from Yemen using laser-based measurements (Baker et al. 2000) illustrates the potential for oxygen isotopes to illuminate the role of even small amounts of crustal contamination in the geochemistry of continental intraplate basalts. Baker et al. compare the  $\delta^{18}\text{O}$  values (and other properties) of green clinopyroxenes that crystallized early in the differentiation history of flood basalts from Yemen to later-crystallizing dark-brown clinopyroxenes in the same rocks. The former were found to have  $\delta^{18}\text{O}$  values similar to those of most primitive basaltic lavas whereas the latter are relatively  $^{18}\text{O}$ -enriched, consistent with progressive contamination by continental crust over the course of crystallization-differentiation. This is an excellent example of the potential power of mineral-specific oxygen isotope analysis to reveal the details of contamination and/or magma mixing processes and will doubtless serve as a model for future studies of similarly complex lavas.

### ARC-RELATED LAVAS

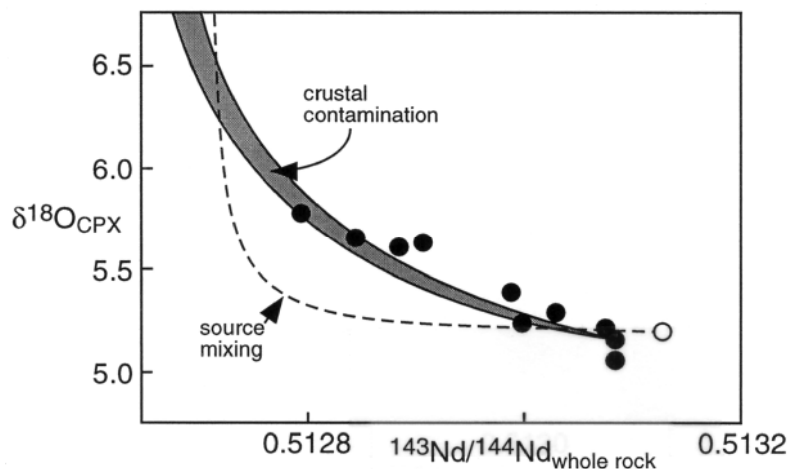
There is unambiguous evidence that the sources of subduction-zone-related volcanic rocks incorporate to greater or lesser degrees the rocks, sediments, and fluids of the down-going plate (Gill 1981). Therefore, the contrast in  $\delta^{18}\text{O}$  between the upper mantle on one hand and various components of old oceanic crust (and their metamorphosed equivalents) on the other could provide a tool for studying the extent and mechanisms of this incorporation. However, convergent-margin igneous rocks are frequently evolved when compared to lavas from other tectonic settings, their evolution often involves complex processes of crystallization and magma mixing that may confound attempts to link phenocryst  $\delta^{18}\text{O}$  to bulk lava properties, and the crust through which they erupt is generally thicker than the oceanic crust and thus offers greater opportunity for contamination than is the case for MORBs and OIBs (Gill 1981).

Therefore arc-related lavas present special opportunities but also special challenges for oxygen isotope studies.

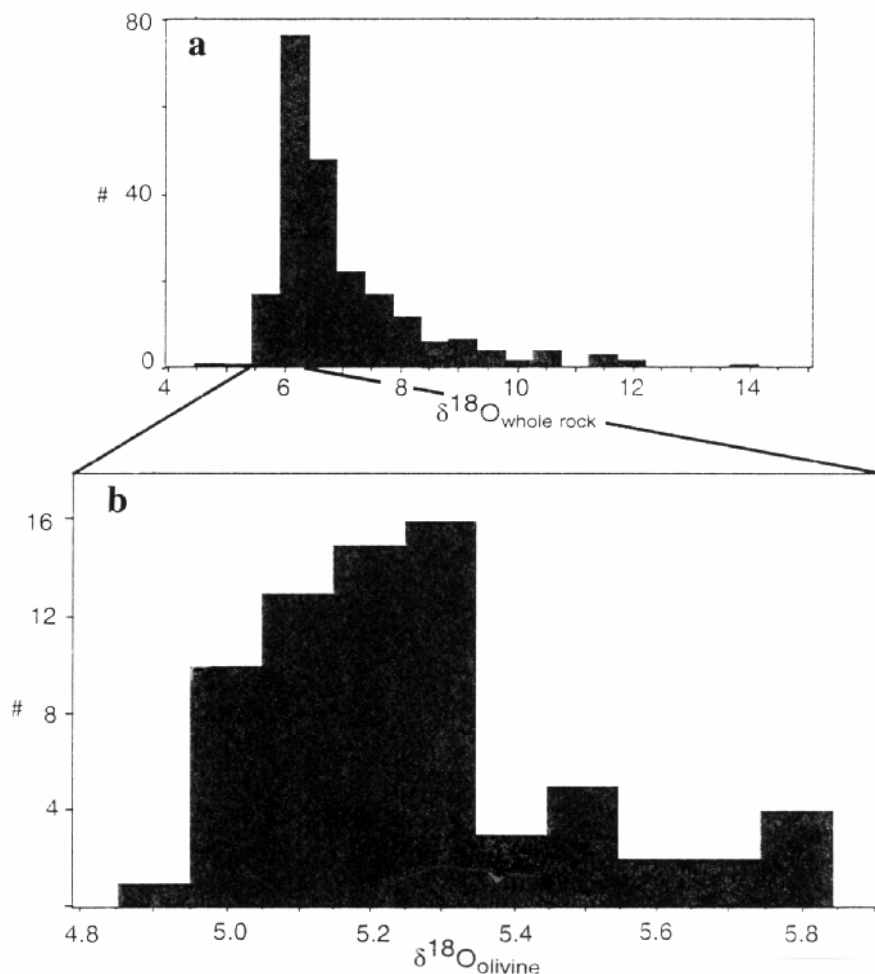
Some of the first comprehensive studies of oxygen isotope variations in island-arc lavas were those of Matsuhisa (Matsuhisa et al. 1973; Matsuhisa 1979), who established that calc-alkaline basalts and basaltic andesites from Japan have  $\delta^{18}\text{O}$  values that are broadly within the range of mafic lavas from other tectonic settings and, thus, that Japanese island arc basalts likely originate by partial melting of peridotites in the mantle 'wedge' rather than by melting  $^{18}\text{O}$ -enriched sediments and altered basaltic rocks in the top of the down-going slab. This is the prevalent view of arc-related magmatism today, but was an important contribution to the debate over the origin of calc-alkaline andesites at the time it was made. These studies also provide one of the best early records of the relationship between  $\delta^{18}\text{O}$  and major-element chemistry among differentiated lavas. The first-order conclusions of the work of Matsuhisa et al. were corroborated by a subsequent study comparing the  $\delta^{18}\text{O}$  of submarine glasses from the Marianas arc and MORBs (Ito and Stern 1985). However, contemporaneous studies (Pineau et al. 1976; Woodhead et al. 1987) suggested that the oceanic arc basalts and andesites are subtly, but systematically,  $^{18}\text{O}$  enriched compared to MORBs due to subducted components in their mantle sources—a conclusion also reached by Harmon and Hoefs (1995) in their review of conventional fluorination data generated up to 1995.

Early studies of variations in whole-rock  $\delta^{18}\text{O}$  provided a somewhat clearer view of the oxygen isotope geochemistry of continental arcs—e.g. the Andes (Harmon et al. 1981)—and oceanic arcs in which the overriding plate is thick and rich in sediments—e.g. the Antilles (Davidson and Harmon 1989). Studies of these systems revealed large ranges in  $\delta^{18}\text{O}_{\text{whole rock}}$  (from values comparable to most terrestrial basalts up to +14 ‰ in several systems) that were correlated with increasing extents of magmatic differentiation and almost certainly reflect crustal assimilation and/or mixing with crustal melts. Recent laser-based studies of mafic lavas from the Andes (Feeley and Sharp 1995), Antilles (Thirlwall et al. 1996) and the Kermadec-Hikurangi arc (Macpherson et al. 1998) corroborate these interpretations (e.g. Fig. 20), suggesting that the oxygen isotope geochemistry of arc-related lavas erupted through thick sequences of sediments and/or continental crust are unlikely to provide information about variations in the  $\delta^{18}\text{O}$  of their mantle sources, but can provide important insights on the evolution and crustal contamination of convergent-margin magmas.

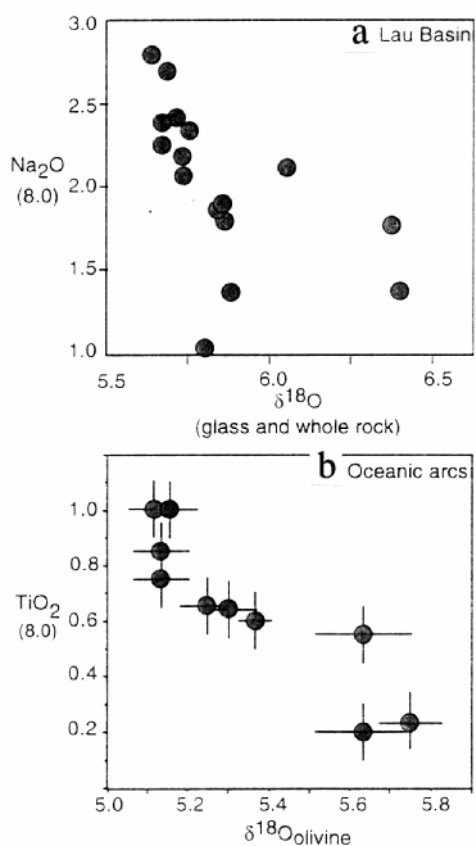
However, use of laser based methods of oxygen isotope analysis to study mafic lavas in arcs has also produced significant differences with the results of previous work. Most simply, the total range in  $\delta^{18}\text{O}$  of phenocrysts in oceanic arc basalts is found to be one-tenth the range observed in whole-rock samples of similar rock types (Fig. 21). Some of this difference must almost certainly be due to the greater diversity of samples in the data base of whole-rock analyses; however, much of this difference is likely due to the fact that analyses of early-liquidus phenocrysts more effectively 'see through' effects of sub-solidus alteration and crystallization-differentiation. Arguably, the most interesting results from recent studies of oxygen isotope variations in convergent margins have come from those focused on mafic lavas from oceanic arcs with thin crust and from back-arc environments. The key result of this work is that values of  $\delta^{18}\text{O}$  appear to increase with decreasing abundance of moderately incompatible elements and, therefore, plausibly with increasing extent of melting of their mantle sources. Figure 22a illustrates this result by comparing  $\text{Na}_2\text{O}$  contents and  $\delta^{18}\text{O}$  values of glasses from the Lau basin (modified from Macpherson and Matthey 1998) and Figure 22b presents a similar comparison of average  $\delta^{18}\text{O}$  values and fractionation-corrected  $\text{TiO}_2$  contents of several suites of lavas from the Marianas, South Sandwich arc and Vanuatu (modified



**Figure 20.** Comparison of  $\delta^{18}\text{O}$  values of clinopyroxenes ('CPX') with  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios of whole rocks for arc-related lavas from the Kermadec-Hikurangi margin; adapted from MacPherson et al. (1998). ● = arc lavas; ○ = inferred composition of clinopyroxene in equilibrium with local depleted mantle. Solid curves are calculated trends for models of magma contamination by continental crust; the dashed curve is the calculated mixing trend between local depleted mantle and subducted upper oceanic crust components. The approximately linear increases in  $\delta^{18}\text{O}$  with decreasing  $^{143}\text{Nd}/^{144}\text{Nd}$  is characteristic of crustal contamination processes.



**Figure 21.** Oxygen isotope compositions of oceanic arc lavas, as measured by (a) conventional fluorination analyses of whole rocks (data compiled by Harmon and Hoefs 1995) and (b) laser fluorination of olivines from mafic lavas (data from Eiler et al. 2000a).



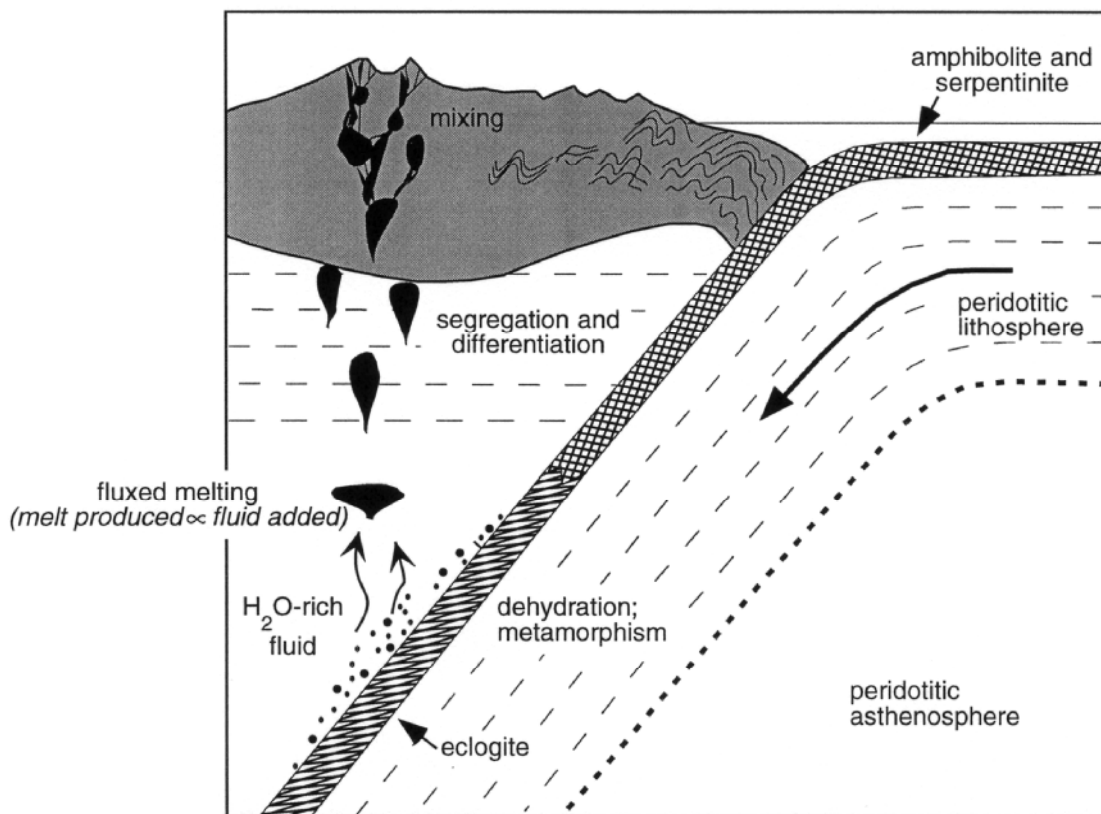
**Figure 22.** (a) Comparison of  $\delta^{18}\text{O}$  of glass or whole rocks from the Lau basin with the fractionation-corrected  $\text{Na}_2\text{O}$  contents of those same rocks; data from Pineau et al. (1976), Vallier et al. (1991), Lichtenstein and Loock (1993) and Macpherson and Matthey (1998). (b) Comparison of the average  $\delta^{18}\text{O}$  of olivine phenocrysts in suites of island-arc tholeiites and calc-alkaline basalts with fractionation-corrected  $\text{TiO}_2$  contents of those same suites; data from Eiler et al. (2000a). Inverse correlations in both (a) and (b) are consistent with increased integrated extents of melting of relatively high- $\delta^{18}\text{O}$  mantle sources; a model of 'fluxed' mantle melting describing such trends is presented in Eiler et al. (2000a).

than stirring of high- $\delta^{18}\text{O}$  recycled crust into the upper mantle; e.g. Indian ocean MORBs are systematically higher in  $^{87}\text{Sr}/^{86}\text{Sr}$  than Pacific and Atlantic MORBs—the so-called 'Dupal' anomaly—but are indistinguishable from other MORBs in average  $\delta^{18}\text{O}$  or relationships between  $\delta^{18}\text{O}$  and minor-element abundances (Fig. 10).

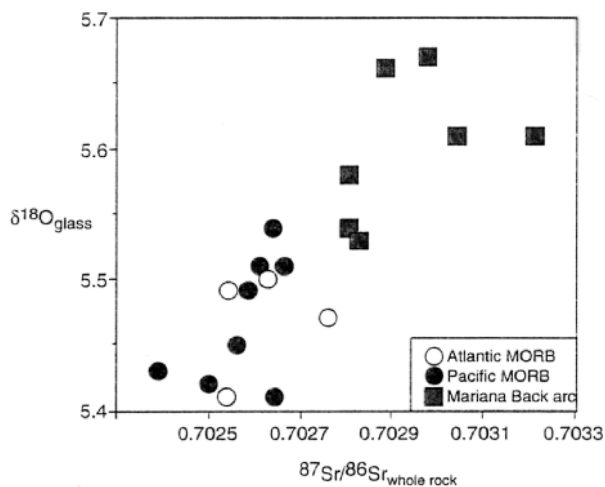
A recent study of mantle xenoliths from a convergent-margin setting found evidence for metasomatism of the sub-arc mantle by  $^{18}\text{O}$ -enriched phases, consistent with the inferences outlined above based on studies of erupted lavas. Eiler et al. (1998) used ion microprobe methods to determine the  $\delta^{18}\text{O}$  values of jadeitic glasses in metasomatic veins in xenoliths from Lihir island, Papua New Guinea, and found them to have  $\delta^{18}\text{O}$  values up to 12 ‰—strikingly  $^{18}\text{O}$ -enriched compared to values of most

from Eiler et al. 2000a). These trends have several possible explanations, but clearly differ from predictions of the effects of peridotite melting alone (Fig. 5) and can be explained by models in which mantle sources of arc lavas initially have  $\delta^{18}\text{O}$  values within the range for MORBs and are 'fluxed' (i.e. driven to melting by addition of components that lower the peridotite solidus) by high- $\delta^{18}\text{O}$ , slab derived fluids (Eiler et al. 2000a; see Fig. 23). This model has features in common with previous explanations of the relationship between water content and elemental abundances in Mariana back-arc lavas (Stolper and Newman 1994) and, like that model, can be used to infer the absolute abundances of minor elements in volatile-rich phases extracted from the down-going slab.

Comparisons between igneous rocks from different tectonic settings are often compromised by confounding variables (e.g. systematic differences in extent and conditions of melting and/or differentiation); nevertheless, Figure 24 shows that MORBs and back-arc basin basalts may define a continuous spectrum of pollution of the upper mantle by subducted components. This figure plots the  $\delta^{18}\text{O}$  values vs.  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios for NMORB glasses from the Pacific and Atlantic oceans and back-arc-basin basalts from the Mariana trough; the results suggest that a subtle but systematic increase in  $\delta^{18}\text{O}$  of the back-arc mantle with respect to NMORB sources accompanies the subtle enrichment of the back arc mantle in radiogenic Sr from the down going slab. This trend resembles the correlation between  $\delta^{18}\text{O}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  defined by the Eiler et al. 1996a, survey of ocean island basalts (Fig. 12), although it is also important to note that there are exceptions to these trends that presumably reflect sources of geochemical enrichment other



**Figure 23.** Schematic illustration of subduction-zone processes that can lead to trends such as those illustrated in Figure 22. Subduction injects hydrated mafic and ultramafic rocks (and accompanying marine sediments) into the upper mantle. Dehydration metamorphism transforms these rocks into eclogitic assemblages with lower water contents, releasing water-rich fluid. This fluid ascends into the mantle 'wedge' (between the over-riding and down-going plates), where it fluxes peridotite melting. The degree of melting is inferred to be proportional to the fluid/rock ratio in the mantle wedge; thus, decreasing concentrations of some incompatible elements ( $\text{TiO}_2$ ,  $\text{Na}_2\text{O}$ ) are associated with oxygen isotope signatures of the subducted slab (typically increasing  $\delta^{18}\text{O}$ ).



**Figure 24.** Comparison of  $\delta^{18}\text{O}$  values for NMORB and back-arc-basin glasses with  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios measured on the same samples; data from Eiler et al. (2000a,b). Indian MORB have been excluded in order to avoid confounding effects of the Dupal anomaly, which is marked by large differences in Sr isotope ratios between Indian MORBs and other MORBs and appears to have no signature in  $\delta^{18}\text{O}$  (Fig. 10).

erupted basalts and consistent with the derivation of the metasomatic melts from a source rich in subducted, upper-crustal oxygen.

Collectively, the recent work on oxygen isotope variations in arc-related rocks suggests that  $\delta^{18}\text{O}$  values of primitive lavas and mantle nodules preserve subtle but

important records of the transfer of subducted components through the mantle wedge and into the volcanic arc, whereas the overprinting influences of crustal contamination dominate oxygen isotope records in more evolved lavas. Naturally, one should expect that these competing processes will interfere with one another in some cases and, thus, future studies will need to exercise caution to make sure the influences of one process (mantle enrichment or crustal contamination) are not ‘mapped’ onto interpretations of the other.

## SUMMARY AND FUTURE DIRECTIONS

### View of the crust/mantle system through stable isotope geochemistry

This chapter began by stating the axioms that lead us to believe oxygen isotope variations of mantle rocks and basalts can provide unusual insights on problems of crustal recycling and lithospheric contamination. So what has this approach shown so far? It is never safe to over-generalize such a broad field, particularly given that it underwent a first-order change in data quality and quantity over the last several years. Nevertheless, the observations presented in the preceding sections suggest the following themes:

- Oxygen isotope variations are closely related to variations in radiogenic-isotope ratios and abundances of trace and major elements in many basaltic systems. Interpretations of these relationships vary from place to place and from time to time as debates evolve; however, the observations themselves are better than would have been imagined five or more years ago.
- There are two ‘styles’ of geochemical enrichment in the earth’s mantle that are commonly associated with lavas having  $\delta^{18}\text{O}$  values higher than those of common peridotites: (1) High concentrations of incompatible minor elements (particularly K) in MORBs; and (2) radiogenic Sr in ocean-island basalts and perhaps back-arc-basin basalts. These phenomena have broadly similar interpretations: Addition of upper oceanic crust and sediment to the mantle raises the abundance of alkali’s and other incompatible elements and increases  $\delta^{18}\text{O}$  in that mantle. Simple mixing relationships in the oxygen-isotope system allow relatively confident estimates of the amounts of recycled material in each case (e.g. ~0 to 5 %, average ~2 %, in the sources of NMORBs, Eiler et al. 2000b; ~2 to 8 %, average ~5 %, in the sources of ‘EM2’ ocean-island lavas, Eiler et al. 1996a).
- Perhaps equally importantly, there are other ‘styles’ of mantle enrichment that are unrelated to oxygen isotope variations, requiring that those enrichments are produced by high-temperature differentiation (metasomatism, melting and crystallization) or by incorporation of only traces (< ~1 %) of subducted crustal material in those regions of the mantle. These include the ‘EM1’ and (with some debate; Thirlwall et al. 1997) ‘HIMU’ types of enriched OIB sources, as well as the ‘Dupal’ anomaly that distinguishes Indian ocean MORBs from other MORBs. It has been common to explain radiogenic-isotope properties of all of these types of enrichment as a consequence of crustal recycling and, therefore, negative evidence from oxygen isotopes creates a dilemma, particularly given the apparent sensitivity of oxygen isotopes to recycled crust in the sources of other types of ‘enriched’ basalts (e.g. ‘EM2’ lavas in Figs. 11 to 13).
- Oxygen isotope variations in magnesian arc lavas from convergent margins erupted through thin crust appear dominated by a processes related to the extent of melting of their mantle sources. The precise balance of adiabatic upwelling vs. ‘fluxing’ of the mantle wedge in producing primary arc magmas is one of the great outstanding

issues in igneous petrology (e.g. Plank and Langmuir 1988; Stolper and Newman 1994) and it appears that oxygen isotopes have something to say about this problem. The existing data can be explained by models of 'fluxed' melting of a static mantle wedge by high- $\delta^{18}\text{O}$  fluids (Eiler et al. 2000a), but alternatives have been suggested (e.g. MacPherson and Matthey 1998, call on the effects of oxygen isotope fractionations between melts and residues) and further tests and refinements of this interpretation are needed.

- There are many environments in which oxygen isotope variations are dominated by crustal contamination. Clear examples include convergent-margin volcanic centers erupted through thick and/or sediment-rich crust, continental intra-plate magmas, central volcano complexes on Iceland, and evolved,  $^{18}\text{O}$ -enriched lavas from the Canary islands. Controversial cases that have also been argued to reflect crustal contamination are subtly  $^{18}\text{O}$ -depleted Hawaiian and Icelandic basalts.
- Our understanding of the oxygen isotope geochemistry of actual mantle rocks is in a state of rapid change. Several studies leave little doubt that most mantle peridotites span a small range in  $\delta^{18}\text{O}$  and are internally equilibrated. However, recent work documents exceptions to this generalization, including the identification of extremely  $^{18}\text{O}$ -enriched metasomatic phases (Eiler et al. 1998) and complex isotopic zonation and  $^{18}\text{O}$ -depletion in re-crystallized and cryptically metasomatized peridotites (Deines and Haggerty 2000; Zhang et al. 2000). It is challenging to concretely link small-scale diversity and complexity of metasomatized xenoliths to compositions of related basaltic lavas, which naturally average out small-scale properties of their sources; however, the connection between these observations and the oxygen isotope geochemistry of basalts is clearly a fruitful area for future research.

### **Outstanding problems and future directions**

The oxygen isotope geochemistry of mantle-derived melts and rocks presents much opportunity for new work simply because the field has undergone a recent revolution in analytical approach, but many easily imagined applications have not yet been done. I conclude this chapter with a list of particularly outstanding research opportunities in this field (based, of course, on the author's prejudices and limitations!); this list could clearly be expanded by adding questions that are raised by recent work described above but not yet explored in detail:

**Experiments.** The experimental basis for interpreting subtle oxygen isotope variations among silicate melts and their phenocrysts is extremely poor, principally because of the lack of data on fractionation factors involving relevant silicate liquids. The directions and magnitudes likely for such fractionations are explored in the first half of this chapter, but without direct experimental constraints it is almost inevitable that misinterpretations of natural oxygen isotope variations have been or will be made. Therefore, new experimental work on this subject is arguably the most important lasting contribution that could be made to this field at this point.

**Subtle secular variations in upper mantle?** There is strong evidence that the isotopic composition of oxygen in the upper mantle has not varied greatly ( $>1\text{‰}$ ) over Earth history (e.g. Kyser 1986), but it is not known whether average mantle  $\delta^{18}\text{O}$  has varied by one or more tenths of per mil. If the  $\delta^{18}\text{O}$  of the upper mantle has changed through time, even subtly, it would be a unique constraint on the integrated history of subduction and, combined with other information, the size of the mantle reservoir into which subducted crust is stirred. This question is naturally made difficult by the subsolidus changes in  $\delta^{18}\text{O}$  undergone by old volcanic rocks and likely diversity in the  $\delta^{18}\text{O}$  of magmas at almost any point in earth history (i.e. 'false positive' results will be easy to



find), but the importance of the problem almost demands that attempts to answer it be made. Insights of this type could provide an important complement to recent constraints on the variation with time of  $\delta^{18}\text{O}$  values of continental granites (Peck et al. 2001).

**Continental flood basalts.** A first-pass has been made at applying laser-based methods to study the oxygen isotope systematics of most major classes of terrestrial basalts. However, continental flood basalts are an exception and the one detailed study that has been made (Baker et al. 2000) suggests that much will be learned by such work.

**Oxygen isotope variations of the Moon and achondrite parent bodies.** There is a long history of taking lessons from the study of terrestrial igneous rocks and applying them to samples from the Moon and the parent bodies of non-chondritic meteorites. Previous work on the oxygen isotope geochemistry of these samples has emphasized mass-independent differences in composition (Clayton and Mayeda 1996); however, a recent study of lunar basalts (Wiechert et al. 2000) indicates that subtle mass-dependant variations in oxygen isotope ratio may have been generated during the evolution of the moon's mantle and it is plausible that similar subtle but coherent 'signals' exist in the oxygen isotope variations of the parent bodies of the SNC ('Martian') and Howardite-Eucrite-Diogenite meteorite clans. These suites provide potentially enlightening points of comparison with the earth's mass-dependent oxygen isotope systematics but are virtually unexplored from this perspective.

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