

Oxygen isotope fractionation among melts, minerals and rocks

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The key factor in interpreting oxygen isotope measurements of natural materials is knowledge of the relative partitioning (or fractionation) of the oxygen isotopes between coexisting phases and its dependence on temperature. Statistical mechanical and empirical chemical-bond calculations stress the importance that cation-oxygen bond type and mineral structure plays in governing the oxygen isotope fractionation behaviour of crystalline materials. The early studies of Taylor and Epstein (1962) and Garlick (1966) on igneous and metamorphic rocks showed that isotopic fractionations in silicates could be substantially understood in terms of linear combinations of the various bond-types (Si-O; Al-O; M-O) present in each silicate structure. An extension of this reasoning is that melts should generally exhibit fractionations similar to their chemically identical crystalline phase, and therefore that the partitioning behaviour of normative major minerals would be sufficient to describe that of melts. On the other hand, naturally occurring partial melts will be compositionally different from their source rocks and thus melt/rock isotopic fractionations could arise from the chemical differentiation during melting. Even so, it has generally been assumed that at the temperatures of

mantle melting, melt/residue fractionation factors will be small (less than a few tenths of a per mil) and not petrologically significant.

This simple view of melt/crystalline solid fractionation behaviour needs to be critically examined. The increased level of detail available using new techniques such as laser fluorination means that effects that were previously unnoticed or too difficult to characterize (such as small isotopic differences between magma types), are now becoming recognized, and they cannot be confidently interpreted without equally detailed understanding of partitioning behaviour.

Figure 1 summarizes the results of experiments we have made 1 atm and 650–950°C on exchange between CO₂ and minerals and melts/glasses of identical composition.

Experimentally measured CO₂–albitic glass/melt and CO₂–crystalline albite are identical within experimental error and preliminary experimental work on the CO₂–anorthitic glass also suggests a close correspondence between the fractionation properties of anorthitic glass and crystalline anorthite. Moreover, the CO₂–glass/mineral fractionation factors for these phases are reasonably well approximated by

TABLE. 1. Oxygen isotope fractionation between crystalline olivine and melts

	Kimberlite	Komatiite	Basanite	Alkali basalt	MORB	low-degree melt ³
Garlick index (I)	0.55	0.58	0.62	0.65	0.70	0.79
A (Ol-melt) ¹	-0.34	-0.54	-0.80	-1.02	-1.35	-1.94
Δ (Ol-melt)@1300°C ²	-0.14	-0.22	-0.32	-0.41	-0.54	-0.78

¹ A is the coefficient in the fractionation equation $1000 \ln \alpha$ (Olivine–melt) = A * $10^6 T^{-2}$. The A value is calculated using the calibration of the Garlick index given by Ganor, J, Matthews, A and Schliestedt, M (1994) *Eur. J. Min.* 6, 365–379, assuming that olivine has a Garlick index of 0.50.

² Δ = δ¹⁸O olivine – δ¹⁸O melt at 1300°C.

³ Low-degree melt of fertile peridotite at ~10 kbar from the experiments of Hirschmann, MM, Baker, MB and Stolper, EM (1998) *Geochim. Cosmochim. Acta* in press.

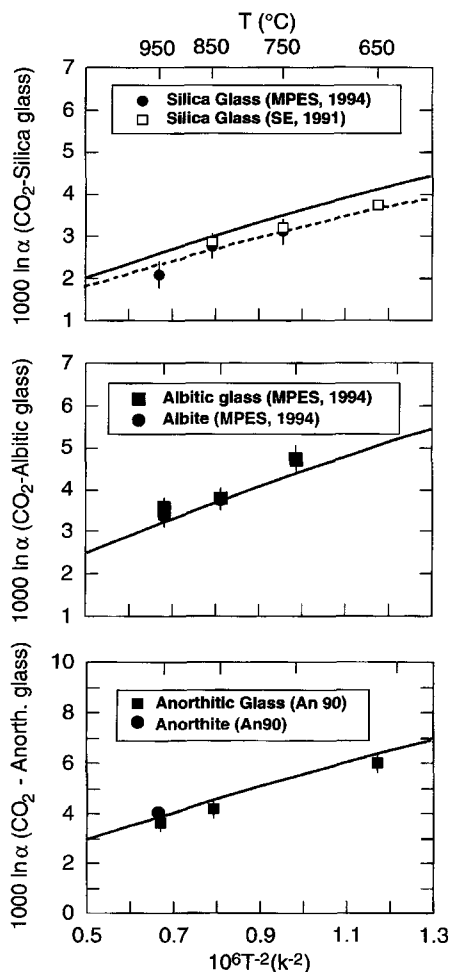


FIG. 1. Experimentally calibrated oxygen isotope fractionation factors determined for exchange between CO_2 and minerals and melts/glasses. Data sources: SE, Stolper and Epstein (1991); MPES, Matthews *et al.* (1994); anorthitic glass/anorthite, this study. Fractionation curves for CO_2 -crystalline mineral partitioning (heavy lines) are calculated from the reduced partition function ratios of Richet *et al.* (1977) for CO_2 and of Clayton and Kieffer (1991) for the minerals.

fractionation curves based on the reduced partition function ratios (rfr) of CO_2 and crystalline albite and anorthite. Thus the view that the isotopic fractionations of melts and glasses approximate those of chemically equivalent crystalline minerals appears to hold for the plagioclase feldspars. In contrast, the experimental CO_2 -silica glass fractionation is significantly less than the fractionation curve based on the rfr of CO_2 and

crystalline quartz and is better fit by a significant (~3.5%) increase of the quartz-rfr (Fig. 1). The short-medium range structures in both silica glass and albitic glass resemble a 'stuffed tridymite' structure, whereas the structure of anorthitic glass has a four-membered ring topology related to crystalline feldspar. Thus, these simple structural factors do not successfully explain the difference in isotopic behaviour between phases in the silica-anorthite-albite system; the reasons for the discrepancy remain unresolved. Without further experimentation, the approximation of comparable solid and melt partitioning should be applied cautiously to natural systems.

The need for additional experimental work is particularly acute for fractionations involving magmas of basic to ultrabasic composition. A wide range of melt compositions can be produced by melting of the mantle (e.g. from kimberlites, to alkaline basalts, to silica-rich melts). Table 1 lists olivine-melt fractionation factors estimated for these compositions at 1300°C , based on the simple 'chemical-bond index' of Garlick (1966). The calculations, though approximate, predict significant variations in the olivine-melt fractionation factor with melt composition, ranging from about -0.1 to -0.2 for ultrabasic melts, to -0.5 for MORB, to -0.8 for alkali-silica rich melts of the sort expected in low-degree melts of fertile peridotite at ~ 10 kbar. The reason for these relatively large predicted variations is that the calculated fractionations depend primarily on the relative proportions of Si-O and Al-O bonds in the melt and the Si/Al ratio varies strongly over the range of melt compositions considered in Table 1. This calculation suggests that these variations cannot be neglected if the isotopic fractionation behaviour of mantle-derived rocks is to be correctly interpreted.

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