Perspectives: Calcium isotope compositions as a means to trace carbonate recycling

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Marine carbonate, an important CO_2 reservoir, is continuously sent to the Earth's deep interior at subduction zones, forming an essential part of the global carbon cycle. We discuss the pros and cons of using calcium isotope compositions to trace marine carbonates recycled into the mantle.

Marine carbonates, such as both sedimentary carbonates and secondary carbonates formed during marine alteration processes, are returned to the mantle at subduction zones, and their fates regulate the global carbon cycle. Some carbonates are destroyed at the subduction zones, contributing to the arc volcanism [1-2]. However, some subducted carbonates may be sampled by intraplate volcanism via mantle plumes or upwelling in big mantle wedge or rift [e.g. 3-4]. Geochemists are exploring novel geochemical and isotopic tools that can be used to trace the recycled carbonate signatures in both mantle derived rocks (basalts) and mantle rocks (peridotites) [see contributions in this issue].

Marine carbonates are mostly $CaCO_3$with ~40 % CaO while the Earth's mantle typically has only 3.5 %CaO. If subducted carbonates have a different Ca isotope composition, measured as $\delta^{44/40}$Ca (= [(^{44}Ca/^{40}Ca)$_{sample}$/(^{44}Ca/^{40}Ca)$_{standard}$ – 1] x 1000), compared to mantle [Figure 1], then $\delta^{44/40}$Ca can be a "smoking gun" for tracing recycled carbonates. This idea led Huang et al. [3] to use $\delta^{44/40}$Ca to estimate the contribution of recycled carbonate in the mantle source of Hawaiian shield lavas.

Recently, Amsellem et al. [5] reported low $\delta^{44/40}$Ca values (~0.6 lower than mantle value) for a global sampling of carbonatites (up to 3 Ga). They argued that the low

$\delta^{44/40}$Ca reflects contributions from surface carbonates recycled into the mantle sources of these carbonatites. However, a subsequent study found that global carbonatites, after screening for alteration, have the same $\delta^{44/40}$Ca range as that shown in silicates [6]. This result is consistent with the finding that peridotites metasomatized by carbonate-rich melt have $\delta^{44/40}$Ca similar to that in unmetasomatized peridotites [7]. In contrast, Banerjee et al. [8] found that the majority of ancient carbonatites (>300 Ma) have mantle-like $\delta^{44/40}$Ca, but some young carbonatites (<300 Ma) have significantly low $\delta^{44/40}$Ca value (~0.5 lower than mantle value).

Both carbonates and silicates have large $\delta^{44/40}$Ca variations, and they largely overlap with each other [Figure 1]. The mantle value has been estimated based on $\delta^{44/40}$Ca in MORBs, peridotites and chondrites, ranging from 0.94 to 1.05 [See Antonelli and Simon [9] for a summary]. This value is close to the average of silicates, 0.89 ± 0.22 [1σ, Figure 1]. It is evident that recycled carbonates can have higher, similar, or lower $\delta^{44/40}$Ca compared to the mantle. If the subducted carbonates have mantle-like $\delta^{44/40}$Ca values, Ca isotope composition cannot distinguish between carbonate and mantle contributions. That is, $\delta^{44/40}$Ca cannot be used to trace carbonate recycling in this case. However, it is unlikely that all subducted carbonates have mantle-like $\delta^{44/40}$Ca values, and $\delta^{44/40}$Ca can be used with other geochemical and isotopic parameters to trace recycled carbonates. This is the approach that we used to identify recycled carbonate in the Hawaiian mantle plume. Specifically, Huang et al. [3] found about 0.3 variation in $\delta^{44/40}$Ca in a group of Hawaiian shield lavas. Importantly, the $\delta^{44/40}$Ca variation is correlated with Sr/Nb and $^{87}Sr/^{86}Sr$, which are also tracers of marine carbonates. These

correlations are best explained by adding up to 4% recycled carbonate into the Hawaiian mantle plume source. In this case, the other two carbonate-sensitive parameter, Sr/Nb and $^{87}Sr/^{86}Sr$, are used to constrain the $\delta^{44/40}Ca$ characteristics of the recycled carbonate sampled by Hawaiian mantle plume. However, the contribution of recycled carbonate estimated using only Sr/Nb and $^{87}Sr/^{86}Sr$ relies on the assumed concentrations of Sr and Nb in the recycled carbonates, which can vary up to several magnitudes. The relative contribution of recycled carbonate is best constrained by $\delta^{44/40}Ca$ using mass balance, because Ca is a major element in carbonates and its content does not vary too much.

Although $\delta^{44/40}Ca$ has the potential to trace carbonate recycling, several issues must be better addressed/understood before making full use of $\delta^{44/40}Ca$. First, there are considerable inter-laboratory differences among published $\delta^{44/40}Ca$ data. For example, published $\delta^{44/40}Ca$ values in the BHVO-1 and BHVO-2 standards range from 0.73 to 0.96 [10], much larger than the typical analytical uncertainty of ± 0.05. As discussed above, three recent studies on global carbonatites [5-6,8] yielded very different results. Sun et al. [6] suggested that the lower $\delta^{44/40}Ca$ in Amsellem et al. [5] might result from the matrix effect of rare earth elements (REEs) that may not be effectively removed during their chemical separation of Ca. However, not all carbonatites studied by Amsellem et al. [5] have high REE contents, and their measured carbonatite $\delta^{44/40}Ca$ does not correlate with REE content. So that the exact reason for such large inter-laboratory difference remains unclear. Nevertheless, the reported large inter-laboratory difference in published Ca isotope studies must be understood and addressed before making full use of $\delta^{44/40}Ca$ data to trace recycled carbonates.

Second, partial melting effects on $\delta^{44/40}$Ca should be better addressed. Using a combination of $\delta^{44/40}$Ca measurements and *ab initio* calculation results, Zhang et al. [11] showed that partial melting of spinel peridotite introduces only a minor effect on $\delta^{44/40}$Ca in melts, which is smaller than typical analytical uncertainty. Instead, large $\delta^{44/40}$Ca effect, of up to 0.3, can be produced in melting residues. Wang et al. [12] found that garnets have higher $\delta^{44/40}$Ca, by 0.1 to 0.4, than their coexisting clinopyroxenes in a series of eclogites and garnet-peridotites from the Dabie-Sulu orogen, China, consistent with the *ab initio* calculation results [13]. Wang et al. [12] also inferred that jadeite-rich clinopyroxene, which is typically stable under high pressure, tends to be enriched in heavy Ca isotopes. Consequently, it is expected that partial melts of garnet peridotite and garnet pyroxenites have lower $\delta^{44/40}$Ca, as observed in the low-Mg adakitic rocks [12]. However, the exact $\delta^{44/40}$Ca effects during partial melting of garnet-bearing lithology are not well constrained. This is because there are no available mineral-melt Ca isotope fractionation factors under high pressures (> 3 Ga) within the garnet stability field. The low pressure mineral-melt Ca isotope fractionation factors inferred by Zhang et al. [11] should not be directly applied to higher pressures, because the structures of minerals and melt respond very differently to pressure. Similarly, the Ca isotopic effects during partial dissolution and breakdown of carbonates, and isotopic exchange among carbonate and silica minerals at subduction zones are also not well constrained due to the lack of reliable mineral-fluid Ca isotope fractionation factors. The mineral-melt/fluid Ca isotope fractionation factors under high pressures must be determined

105 experimentally and/or by *ab initio* calculations before making full use of $\delta^{44/40}$Ca data to
106 trace recycled carbonates.

107 Last, kinetic processes can also fractionate Ca isotopes. Zhao et al. [14] found very
108 low $\delta^{44/40}$Ca, down to -0.1, in some peridotite xenoliths from the North China Craton,
109 and they attributed the low $\delta^{44/40}$Ca as a result of melt-rock reaction that occurred at
110 the base of the lithospheric mantle. Specifically, lighter Ca isotopes are preferentially
111 incorporated into clinopyroxene during melt-mantle reaction. Antonelli et al. [15]
112 reported low $\delta^{44/40}$Ca in both natural and experimentally grown plagioclases, and they
113 attributed the low $\delta^{44/40}$Ca in plagioclases as a result of kinetic effects during magmatic
114 plagioclase crystallization. Additional geochemical and isotopic tracers must be used
115 together with $\delta^{44/40}$Ca to distinguish among recycled carbonates, metasomatized
116 mantle, and plagioclase cumulates.

117 In summary, because of the large $\delta^{44/40}$Ca variation in carbonates compared to the
118 mantle, and the large CaO concentration difference between marine carbonates and the
119 mantle, the Ca isotope composition is a potentially powerful tool for tracing recycling of
120 carbonates into the mantle, especially when used in combination with other
121 geochemical and isotopic tracers for carbonates [see contributions in this issue].
122 However, there remain some problems that should be addressed: 1. large inter-
123 laboratory differences in Ca isotopic measurements; 2. a better understanding of Ca
124 isotopic effects during igneous, metasomatic, and metamorphic processes, including
125 under high pressures, using analytical, experimental and theoretical approaches.
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Figure 1. Histogram of $\delta^{44/40}$Ca in carbonates and silicates. Although carbonates have a lower average than silicates (0.61 ± 0.36 (1σ) vs. 0.89 ± 0.22 (1σ)), the $\delta^{44/40}$Ca distributions in carbonates and silicates largely overlap. The estimated mantle values ranges from 0.94 to 1.05 [See Antonelli and Simon [9] for a summary], which is close to the average silicate value. We note that the highest and the lowest $\delta^{44/40}$Ca in silicates are found in mantle rocks: USGS standard samples DTS-1, -2 (Twin Sisters dunite) and Fe-rich peridotitic xenoliths from North China Craton [14], respectively. As a consequence, the average silicate $\delta^{44/40}$Ca value is close to, if not representative of, mantle value. Data are from the compilations in Refs. 11 and 16.