CHALLENGE ON $^{48}$Ca ENRICHMENT
FOR CANDLES DOUBLE BETA DECAY EXPERIMENT

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Chemical isotope effects of calcium were studied by liquid-liquid extraction using a crown ether of dicyclohexano-18-crown-6 for the purpose of finding a cost-effective and efficient way of enrichment of $^{48}$Ca towards the study of the neutrinoless double beta decay ($^{0\nu}\beta\beta$) of $^{48}$Ca. We evaluated each contribution ratio of the field shift effect and the hyperfine splitting shift effect to the mass effect of the calcium isotopes for the first time. The present preliminary result suggests the contribution of the field shift effect is small, especially for $^{40}$Ca–$^{48}$Ca case, compared with the case of Chromium trichloride-crown in which the isotope enrichment factors are strongly affected by the field shifts. These indications are promising towards the mass production of enriched $^{48}$Ca by the chemical separation method.

1 Double Beta Decay of $^{48}$Ca and Chemical Separation of Calcium Isotopes

Among $\beta\beta$ isotopes, the Q-value of $^{48}$Ca is the highest (4.27 MeV), which is far above energies of $\gamma$-rays from natural radioactivities, therefore our measurement is not limited by backgrounds in the energy region at 4.27 MeV. We have developed a CaF$_2$ scintillation detector system (ELEGANT VI) which is an experiment with an “active source” (source=detector) containing $^{48}$Ca target source inside, being operated at the underground laboratory (Oto Cosmo Observatory) in Nara. For further improvements, we are now developing a new detector system CANDLES (CAlcium fluoride for the study of Neutrinos and Dark matters by Low Energy Spectrometer) sensitive to the half-life of $10^{26}$ yr for neutrinoless double beta decay ($^{0\nu}\beta\beta$) of $^{48}$Ca ($< m_{\nu} >$~0.03 eV), which ultimately requires several tons of calcium. The only drawback of $^{48}$Ca in terms of $^{0\nu}\beta\beta$ is a small natural abundance of 0.187%.

Now the widest variety of stable isotopes are mainly produced at electromagnetic separators and gas centrifuges. Practically the separation of stable isotopes of calcium is presently being accomplished with electromagnetic separators (calutrons) at Oak Ridge National Laboratory and Russia. The rare calcium isotopes separated by this method are expensive, and their use is often limited by cost. Unfortunately flexible highly efficient centrifugal technology is only possible for those elements (about 20) which have gaseous compounds at room temperature.

*Enriched calcium is commercially available as carbonate or oxide by TRACE Science Int., but the cost is expensive ($\sim$ 200K$/g$) and the amount is limited with only a few grams.
Therefore, these methods cannot meet the production of some ββ isotopes such as $^{48}$Ca, $^{96}$Zr and $^{150}$Nd etc. The present paper shows our initial attempt toward the enrichment of $^{48}$Ca and its preliminary result on the separation of calcium isotope by utilizing calcium isotope effect in liquid-liquid extraction (LLE) of calcium chloride using a crown ether. The first publication on the chemical isotope separation with macrocyclic polyether was calcium isotope separation with dicyclohexano-18-crown-6(DC18C6)². Isotopic enrichment occurs according to the following chemical exchange reaction:

$$^{40}\text{Ca}^{2+}_{(aq)} + ^{48}\text{Ca}L^{2+}_{(org)} \rightarrow ^{48}\text{Ca}^{2+}_{(aq)} + ^{40}\text{Ca}L^{2+}_{(org)}$$  \hspace{1cm} (1)

where $L$ represents macrocyclic polyether(18-crown-6). As a result, $^{40}$Ca is enriched in the organic-phase(org) crown solution and the heavy isotopes of $^{48}$Ca tend to concentrate in the aqueous(aq) phase.

2 Experimental

Dicyclohexano-18-crown-6 was obtained from Aldrich Chemical Company (98% purity). Chloroform (99% purity) and Calcium chloride (95%) were products of Nacalai Tesque. Calcium chloride was dissolved in pure water to create a solution, 3M CaCl$_2$. This solution served as the aqueous phase. The organic phase was 0.07M DC18C6 in chloroform. A 20 ml aqueous solution and 200 ml organic solution were mixed in a flask. The two phases were stirred by a magnetic stirrer for 1 h and allowed for standing. This procedure was carried out at 280 K. After the two phases were separated, the upper aqueous phase was taken. It is noted that before the above procedure, we did a vacant-extraction by using a pure water to reduce impurities. Presently the same liquid-liquid extraction experiment was iterated six times.

3 Isotope Analysis

The fractionation of $^{48}$Ca from the most abundant isotope $^{40}$Ca (96.9%) is the key to realize the chemical separation method by liquid-liquid extraction using a crown ether. Unfortunately the most abundant $^{40}$Ca cannot be measured even by high resolution double-focusing sector field ICP-SFMS (HR-ICP-MS; JMS-Plasmax 2) at the Wakasa Wan Energy Research Center, where $^{43}$Ca, $^{44}$Ca and $^{48}$Ca can be measured⁴, because the coincidence of $^{40}$Ar$^+$ and $^{40}$Ca is the most annoying example of an isobaric interference and its required resolution(192498) is beyond this ICP-MS's maximum resolution (12000). In order to measure concentrations of $^{40}$Ca, reaction-cell ICP-MS(Perkin Elmer-SCIEX, ELAN DRCII) was used at the Center for Advanced Marine Core Research, Kochi University. Gas selection is an important component of interference reduction. The ELAN DRC system allows use of more effective reaction gases such as ammonia that reduces the $^{40}$Ar$^+$ interference for $^{40}$Ca by a factor of 10$^9$, compared to a factor of 10$^3$ obtained by a simple “collision” cell ICP-MS, which must use simple collision gases, such as hydrogen and helium, to limit the formation of adverse side reaction products. The isotope abundance at 40, 43, 44, 48u were measured with ammonia gas flow of 0.5 ml/min and nebulizer flow of 0.1 ml/min. The measured relative deviation from “Cica” 1000 ppm AAS standard (as a standard solution) of $^{40}$Ca, $^{43}$Ca, $^{44}$Ca and $^{48}$Ca are shown in Fig. 1(Left). The precision of measured isotopic ratios was about 0.2~0.1% (1 $\sigma$).

The $^{40}$Ca fractionation was successfully measured, but the measured separation factor is a bit small, compared with the previous ICP-SFMS’s data. Much more precise isotope analysis is essential for this confirmation and now we are on our way to verify this by using TIMS(Thermo Electron Corp., TRITON) with a double-spike technique to correct instrumental mass bias and instrumental drifts.
4 Calcium Isotope Effect

In the following, we will use the data from reaction-cell ICP-MS only for the consistency. Now we can evaluate the isotope effect quantitatively by utilizing the new Bigeleisen theory reported in 1996[5]. The isotope effect in the chemical exchange reaction can be written in terms of three effects such as the nuclear mass effect, the nuclear size and shape effect, and the contribution of hyperfine splitting based on the nuclear spin in the simple equation as follows, based on his new theory;

\[
\ln \alpha = a(\Delta M/MM') + b\delta < r^2 > + \ln K_{hf},
\]

where \( M \) and \( M' \) are the nuclear masses of isotopes, respectively, and \( \Delta M \) is the mass difference of isotopes, and \( \delta < r^2 > \) and \( \ln K_{hf} \) are the change in the mean square of the charge distribution radii[3] and the contribution of hyperfine splitting based on the nuclear spin, respectively. The scaling factors of the nuclear mass effect and that of the nuclear size and shape effect, namely the field shift effect, are represented by \( a \) and \( b \), respectively. By using Eq.(2), we can evaluate each contribution of these three effects to the total calcium isotope effect. There are three free parameters, then we need three sets of equations to get each contribution. Here, our primary concern is to obtain each contribution ratios relative to \( {}^{48}\text{Ca} \) between the field shift effect, the mass effect, and the hyperfine splitting shift effect. Thus, we use the three isotope pairs of calcium, \( {}^{40}\text{Ca} - {}^{48}\text{Ca}, {}^{44}\text{Ca} - {}^{48}\text{Ca}, {}^{43}\text{Ca} - {}^{48}\text{Ca}, \)

\[
\epsilon_{40-48} = a(\Delta M/MM')_{40-48} + b\delta < r^2 >_{40-48},
\]

\[
\epsilon_{44-48} = a(\Delta M/MM')_{44-48} + b\delta < r^2 >_{44-48},
\]

\[
\epsilon_{43-48} = a(\Delta M/MM')_{43-48} + b\delta < r^2 >_{43-48} + (\ln K_{hf})_{43}.
\]

The isotope separation factor \( \alpha \) and the isotope enrichment factor \( \epsilon \) are defined as follows;

\[
\alpha_{M-48} = ([{}^M\text{Ca}]/[{}^{48}\text{Ca}])_{org}/([{}^M\text{Ca}]/[{}^{48}\text{Ca}])_{aq},
\]

\[
\epsilon_{M-48} = \alpha - 1,
\]

where \( ([{}^M\text{Ca}]/[{}^{48}\text{Ca}])_{org} \) and \( ([{}^M\text{Ca}]/[{}^{48}\text{Ca}])_{aq} \) are the isotopic ratios of \( {}^M\text{Ca} \) to \( {}^{48}\text{Ca} \) in the organic phase and that in the aqueous phase, respectively. The superscript \( M \) means mass number 40, 44, 43, or 48. Since the isotope enrichment factor, \( \epsilon_{M-48} \) is the dimensionless, we will use the relative values of \( (\Delta M/MM')_{M-48} \) and \( \delta < r^2 >_{M-48} \).

The values of each contribution of \( a, b \) and \( \ln K_{hf} \) are calculated using sequential equations and compared with \( \text{CrLCl}_3 \) case, which was measured (and evaluated) by T. Fujii et al.[7]. Thus, we can estimate each contribution ratios of the field shift effect to the mass effect for the above three isotope pairs, which is summarized in Table 1, in comparison with the case of Chromium trichloride-crown(DC18C6). This preliminary result shows that the ratios of the field shift effect to the mass effect are small, especially for \( {}^{40}\text{Ca} - {}^{48}\text{Ca} \) case, compared with the \( \text{CrLCl}_3 \) case. This is crucial asset in order to realize the \( {}^{48}\text{Ca} \) enrichment by utilizing this chemical separation method, because \( {}^{40}\text{Ca} \) is the largest abundance isotope and if the field shift effect (the nuclear size and shape effect) is dominant, which is shown in filled points and lines from the nuclear charge radii in Fig. 1(Left), this chemical separation method is not effective for the separation of \( {}^{48}\text{Ca} \) from the most abundant \( {}^{40}\text{Ca} \). This preliminary quantitative result on calcium isotope effect is in contrast to the previously obtained experimental data of chromium isotope effect[7]. Chromium isotope has a similar characteristic “parabolic” nuclear charge distribution to the calcium isotope, which are shown as filled points and lines in Fig. 1(Right). This is because \( {}^{52}\text{Cr} \) has the smallest nuclear charge radius due to its the same magic number neutrons \( N = 28 \).
as $^{48}\text{Ca}$. They found a clear mass-independent isotope effect that the medium $^{52}\text{Cr}$ is foremost fractionated according to the Bigeleisen theory. The notable difference between Cr isotopes and Ca isotopes is that the latter has two doubly magic isotopes $^{40}\text{Ca}$ and $^{48}\text{Ca}$ and these also have a magic number of neutrons.

Table 1: Contribution ratios of the field shift effect or the hyperfine splitting shift effect to the mass effect for $^{40}\text{Ca}$, $^{44}\text{Ca}$, and $^{43}\text{Ca}$ relative to $^{48}\text{Ca}$, in comparison with that for $^{50}\text{Cr}$, $^{54}\text{Cr}$, and $^{53}\text{Cr}$ relative to $^{52}\text{Cr}$.

| Isotope     | Contribution Ratio | Concentration of Neutrons |
|-------------|--------------------|---------------------------|
| $^{40}\text{Ca}$ - $^{48}\text{Ca}$ | 0.02±0.48          |                           |
| $^{44}\text{Ca}$ - $^{48}\text{Ca}$ | 0.62±1.31          |                           |
| $^{43}\text{Ca}$ - $^{48}\text{Ca}$ | 0.22±0.88          | 0.64±1.35                 |
| $^{50}\text{Cr}$ - $^{52}\text{Cr}$ | 1.12±2.79          |                           |
| $^{54}\text{Cr}$ - $^{52}\text{Cr}$ | -2.81±5.97         |                           |
| $^{53}\text{Cr}$ - $^{52}\text{Cr}$ | -2.05±8.94         | -0.83±6.17                |

Figure 1: Left: Observed calcium isotope effects (left axis) and experimental values for the mean square nuclear charge radii (right axis) of the calcium isotopes relative to $^{44}\text{Ca}$. Filled (line) and open (dotted line) points correspond to nuclear charge radii and our obtained data, respectively. The dashed line is the expected mass effect, which shows a linear relationship with mass number. Right: Previous studies on chromium isotope effects (left axis) and experimental values for the mean square nuclear charge radii (right axis) of the chromium isotopes relative to $^{52}\text{Cr}$. Filled (line) and square (dotted line) points correspond to nuclear charge radii and the experimental data measured by T. Fujii et al. respectively.

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