

## Synthesis of oxygen isotope-enriched oxides by hydrothermal reaction of metals and water

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In order to fully understand local structure of silicate melts/glasses, we need to study them from not only from cation based viewpoint, but also from anion based viewpoint.  $^{17}\text{O}$  NMR is one of good techniques for this, and could provide structural information around oxygen in the structure. However, this technique has not been fully employed in past. One of major obstacles for its use is that natural abundance of  $^{17}\text{O}$  is very low. Therefore, we have to use  $^{17}\text{O}$  enriched material for solid  $^{17}\text{O}$  NMR studies. In order to produce  $^{17}\text{O}$  enriched starting materials, several synthesis techniques have been used, but most of techniques require complicated chemical procedures and/or toxic chemicals. Also initial high  $^{17}\text{O}$  ratio of reagent (e.g., water) will be diluted during these processes. Recently Schmidt et al. (Solid State NMR, 26, 197, 2004) has developed a novel technique which utilize hydrothermal reaction of metal and enriched water, and applied for  $\text{Al}_2\text{O}_3$ . This technique is superior than previous ones, since all oxygens in enriched water are used to form oxide without reducing high  $^{17}\text{O}$  ratio of original enriched water. Also the technique is simple, and easy to adapt for experimental lab which has hydrothermal reactor. In this study, we applied this technique to other oxides, MgO, CaO and  $\text{SiO}_2$ , and results are reported below.

For hydrothermal reaction, we used an ordinary cold-seal bomb. Metal and water are sealed in Pt capsule. For Si, the run condition was 500 and 600°C, 1kb and 2 to 4 days. There was still unreacted Si found with white powder in 500°C run, but Si was significantly reduced in the product at 600 °C. A bit higher temperature and/or longer run duration will result complete conversion. The white powder was a mixture of quartz and cristobalite, with more cristobalite in lower temperature run. For Mg, the run condition was 500°C, 1kb and 4 days. We observed complete conversion to MgO with some brucite. Brucite was formed, because initial water content was few % excess than nominal MgO composition. For Ca, reaction with  $\text{H}_2\text{O}$  is very rapid at ambient condition, so no hydrothermal run was conducted. Instead, Ca metal is put in a glass bottle, and water is slowly added until all metal reacts. White powder was obtained in this way. However, condition for synthesis is difficult to control, so we did additional experiment using  $\text{CaSi}_2$  as a starting material. In this case, run condition was similar to Si, and white powder was produced. We have not well characterized this powder yet. We also tried Al to confirm Schmidt et al (2004) result. Although our experimental pressure and temperature (1kb, 500°C) were lower than their study (3kb, 600°C), we could get complete conversion from Al metal.

From present study, we have demonstrated that  $\text{SiO}_2$ , MgO and  $\text{Al}_2\text{O}_3$  can be produced from metal plus water by hydrothermal technique. For Ca, after reaction at ambient condition, further reaction in hydrothermal reactor to completely convert it to  $\text{Ca}(\text{OH})_2$  would be possible. Alternatively, we could use  $\text{CaSi}_2$ , if CaO content is not high. So now we can synthesize samples in the CaO-MgO- $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  system without reducing initial high  $^{17}\text{O}$  isotope ratio. We plan to use this technique to produce  $^{17}\text{O}$  enriched silicate glasses and high pressure crystals for  $^{17}\text{O}$  NMR studies in near future.