

## Applications of neutron diffraction studies at LANSCE to environmental and energy problems

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Time-of-flight (TOF) neutron diffraction (ND) with Rietveld refinement is a powerful tool for investigating materials of interest in environmental and energy science. The high-pressure preferred orientation (HIPPO) beamline coupled with a torroidal anvil press or high-P low-T gas/liquid cells allow determination of EOS and D positions of D-bearing phases as f(P,T). Recent investigations at Los Alamos Neutron Science Center (LANSCE) have focused on a range of energy/environmentally relevant materials.

Jarosite (KFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>) structure was investigated using TOF ND from room T to its dehydroxylation T. With increasing T its c axis expands 10 times more rapidly than its a axis. Fitting of cell volumes yields  $\alpha = \alpha_0 + \alpha_1 T$  with  $\alpha_0 = 1.01 \times 10^{-4} \text{ K}^{-1}$  and  $\alpha_1 = -1.15 \times 10^{-7} \text{ K}^{-2}$ . H bonds holding the (001) octahedral-tetrahedral sheets together are weakened with increasing T. Near the dehydroxylation T, jarosite decomposes into yavapaiite and hematite (+ vapor).

H clathrate has potential as a H storage material. TOF ND at low T (10-300 K) and high P (1-2000 bar) show: 1) large cages of the SII clathrate structure reversibly varies from 2 to 4 D<sub>2</sub> molecules with decreasing T while the small cage contains a single D<sub>2</sub> molecule over the full T range; 2) D<sub>2</sub> are localized in both cages of the SII clathrate structure at low T and become delocalized in both cages at higher T; 3) there is shortening of D-D bonds in the clathrate cages, with bond lengths shorter than in metallic H.

Studies of molecular organic framework (MOF) compounds potentially useful for H<sub>2</sub> storage or gas separation reveal D<sub>2</sub> positions and crystal structures. We studied H adsorption in Cu<sub>3</sub>[Co(CN)<sub>6</sub>]<sub>2</sub>, a Prussian blue analogue, at 10 MPa of D<sub>2</sub> from 40 to 200 K. Cell volume increases from 990.5(4) Å<sup>3</sup> under vacuum to 993.5(3) Å<sup>3</sup> at 10 MPa, implying incorporation of significant amounts of D<sub>2</sub> into the nanoporous framework. In addition, we synthesized a highly stable porous lanthanide MOF, Y(BTC)(H<sub>2</sub>O)·4.3H<sub>2</sub>O, and ND of the dehydrated phase revealed four distinct D<sub>2</sub> sites that are progressively filled within the framework.

## Incomplete mixing of nucleosynthetic components in Ba isotopes of primitive chondrites

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Heterogeneous isotopic compositions observed in several elements of carbonaceous chondrites support the incomplete mixing model of some nucleosynthetic components in the early solar system. Barium is one of promising elements to address the details of nucleosynthesis and presolar grain formation of the solar system [1-3]. Barium has seven stable isotopes with the mass numbers 130, 132, 134, 135, 136, 137 and 138. <sup>130</sup>Ba and <sup>132</sup>Ba are p-process isotopes produced by photodisintegration, <sup>134</sup>Ba and <sup>136</sup>Ba are s-only process isotopes, and <sup>135</sup>Ba, <sup>137</sup>Ba and <sup>138</sup>Ba are s- and r-process isotopes. In addition, <sup>135</sup>Ba isotopic abundance may be affected by decay from presently extinct <sup>135</sup>Cs isotope (t<sub>1/2</sub>=2.3 Ma), which can be used for Cs-Ba geochronological application [3,4].

Ba isotopic compositions of chemical leachates from eleven carbonaceous chondrites, Orgueil (CI) Mighei (CM2) Murray (CM2) Murchison (CM2) Sayama (CM2) Allende (CV3) Efremovka (CV3) Isuna (CO3) Kainsaz (CO3) Maralinga (CK4) and Karoonda (CK4) were determined by thermal ionization mass spectrometry to assess the chemical evolution in the early solar system. The barium isotopic data in most of the leachates show variable <sup>135</sup>Ba excesses correlated with <sup>137</sup>Ba excesses, suggesting the presence and heterogeneity of additional nucleosynthetic components for s- and r-processes in the solar system. The isotopic deviation treated in this study are generally small (-3<ε<+3). As exceptional cases, large deviations of <sup>135</sup>Ba (ε=-13.5 to -5.0) and <sup>137</sup>Ba (ε=-6.2~-1.2) observed in the acid residues from one CI and four CM meteorites show significant evidence for enrichments of s-process isotopes derived from presolar grains. Subtraction of s- and r-isotopic components from the total Ba isotopes of CM meteorites allows us to consider the possible existence of presently extinct <sup>135</sup>Cs isotope in the early solar system.

[1] Ranen and Jacobsen (2006) *Science* **314**, 809-812.

[2] Carlson *et al.* (2007) *Science* **316**, 1175-1178.

[3] McCulloch and Wasserburg (1978) *Ap.J.* **220**, L15-L19.

[4] Hidaka *et al.* (2003) *EPSL* **214**, 455-466.