Pressure-induced phase transitions and electron spin state changes of iron bearing spinels

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High-pressure phase transitions of iron bearing spinel compounds in the earth crust attract a large attention in order to understand strong electronic correlation such as charge transfer, electron hopping, electron high-low spin transition, Jahn-Teller distortion and charge disproponation in the lower mantle or subduction zone. To prove the Jahn-Teller transition and electron spin state change of Fe_3O_4, Fe_2TiO_4, $FeCr_2O_4$ and Fe_2SiO_4, we executed a series of the diffraction studies of these polycrystalline and single-crystal and X-ray emission study (XES) using DAC and SR facilities at ambient temperature and Raman spectroscopic study under high pressures up to 90GPa.

Fe_2TiO_4 and $FeCr_2O_4$ show the transformation from cubic (*Fd3m*) to tetragonal ($I4_1/amd$) with c/a<1.0 and transform to orthorhombic (*Cmcm*) due to the Jahn-Teller effect of Fe^{2+} ($3d^6$) at the tetrahedral site[1]. The transition to orthorhombic post-spinel structure at high pressures is confirmed in these whole solid solutions. The transition pressures decrease from 27GPa (Fe_3O_4) to 12GPa (Fe_2TiO_4) with increasing Ti content.

XES reveals the spin transition between high spin (HS) and low spin (LP). The transition pressures of Fe_5O_4, Fe_2TiO_4, Fe_2SiO_4 are 22GPa, 18GPa and over 80GPa, respectively. The HP-LP transition induces their structure transitions due to the enormous reduction in iron ionic radius. A new further high-pressure phase (*Pmma*) of Fe_2TiO_4 was found. Rietveld analyses of the powder diffraction data have been conducted and the bulk modulus of each phase was observed.

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Boron contents and isotope compositions of oceanic crusts from the Oman and Troodos ophiolites

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Boron is excellent tracer for elucidating crustal recycling in subduction zones because of the high concentration of boron in the upper part of the slab and the high mobility of boron during dehydration of the slab. However, fundamental data for vertical distribution of boron in hydrothermally altered oceanic crust are still limited. In this study, boron contents and isotopic compositions were determined for complete section of the oceanic crusts in the Oman and Troodos ophiolite.

Although the boron contents of rocks decreased with depth in both the oceanic crusts, altered rocks from deep section showed obvious boron enrichment relative to fresh rocks. The pillow lavas in the Troodos ophiolite, which have been weathered on the seafloor for ~80 Myrs, was highly enriched in boron (>100 ppm), supporting that boron inventory of pillow lava section strongly depends on the crustal age. The $\delta^{11}B$ of rocks in the Oman ophiolite systematically increased with depth and negatively correltate with the $\delta^{18}O$ values, suggesting that the $\delta^{11}B$ values are eccentially controlled by alteration temperature. On the othre hand, the $\delta^{11}B$ profile in the Troodos ophiolite didn't show clear increase trend.

The boron contents for the bulk oceanic crusts of the Oman and Troodos ophiolites are estimated to be 3.6 ppm and 12 ppm, respectively. About 8‰ of $\delta^{11}B$ was estimated for both the bulk oceanic crusts. In contrast to previous views, hydrothermally altered gabbro section can be a large sink of boron. This boron-enriched, high-$\delta^{11}B$ lower oceanic crust may impact on the estimate of the $\delta^{11}B$ value for fluids librated from the subducted oceanic slab, which is believed to largely control the $\delta^{11}B$ values of arc magmas generated in the mantle wedge.