Phase diagram and structure transition of Fe_3O_4-Fe_2TiO_4 solid solution under pressures up to 60 GPa

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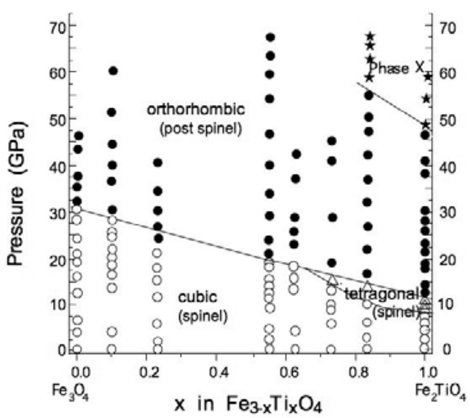
The solid solutions between Fe_3O_4 magnetite and Fe_2TiO_4 ulvöspinel are principal magnetic materials in the crust, which are very similar to $Fe_{3-x}Si_xO_4$ [1][2]. Fe_3O_4, is ferrimagnetic and Fe_2TiO_4 is antiferromagneic.. High-pressure powder diffraction experiments of $Fe_{3-x}Ti_xO_4$ at pressures up to 60 GPa have been performed using synchrotron radiation. The high-pressure transition from cubic spinel to orthorhombic post-spinel structure is confirmed in the whole compositional range. The transition pressure decreases from 27 GPa (x=0.0) to 12 GPa (x=1.0) with an increase in the Ti content (Fig. 1)



The solid solutions with $0.734 \leq x \leq 1.0$ show the transition from the cubic to the tetragonal spinel. The transition pressures are 12 GPa at x=0.734 and 8 GPa at x=1.0. This transition is due to Jahn-Teller effect of Fe^{2+} ($3d^6$) .The tetragonal phase is not observed in the samples with x<0.624. An unknown phase at x=1.0 was found at 48 GPa.

The bulk modulus of spinel phase is calculated by the Birch-Murnaghan EOS. The modulus becomes larger with increasing Ti substitution for Fe.: 183.4(8.1) GPa for Fe_3O_4 and K_0=238.1(4.2) GPa for Fe_2TiO_4.

[1]Yamanaka & Okita (2001) *Phys Chem Miner* **28**, 102-109.
[2]Yamanaka *et al*. (2001) *Phys Chem Miner* **28**,110-118.

Geochemistry and hydrogeology of a marine shallow-water hydrothermal system at the Wakamiko submarine crater, Japan

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Marine shallow-water hydrothermal activity was discovered at the Wakamiko submarine crator of 200 meters water depth in Kagoshima Bay. The Wakamiko crator is considred as a volcanic vent of a giant eruption at 25ka representing the last stage of the Aira caldera formation. At present, most part of the Aira caldera of 30 km x 20 km in size is submerged to be a part of Kagoshima Bay, which shorelines are bordered by the rim.

We collected hydrothermal fluids (T = 200°C) venting from chimney-like structures on the crator floor, during NT07-09 and NT07-16 dive missions conducted using ROV *Hyper Dolphine* (Japan Agency for Marine Science and Technology). The fluid chemistry is explained by hydrothermal interactions between seawater and felsic volcanic material, although the Cl concentration was only half of seawater. The isotopic composition characterized by significantly negative δD value suggests involvement of meteoric water as the fluid origin.

To confirm recharge of meteoric water into the fluid circulation sytem, we collected some hot spring waters (T = 40 - 80°C) close to the shore line, which are pumped up from reservoirs situated at 650 - 1100 m deep. Relationship between Cl concentration and δD value of the spring waters was well accordance with a mixing trend between the seawater and local ground water, which covers the data of the submarine vent fluid.

Previous geological studies implies that the hot spring reservoirs distribute in pyroclastic flow layers which piled prior to the Aira caldera formation. It is reasonable to expect that the submarine discharge of the hydrothermal fluid originated from a reservoir in the same sediment layer. Geophysical studies confirms a magma chamber about 10 km beneath the Wakamiko crator. It is reasonable to expect that a fluid circulation system of 30 km in a diameter is driven by the present active magma chamber.