

博士論文

Chemical property of subduction-zone fluids:
Experimental study on mineral solubility and aqueous speciation
at high pressure and temperature

(沈み込み帯流体の化学的性質：
高温高圧下における鉱物の溶解度と溶存化学種に関する実験的研究)

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Abstract

Subduction-zone fluids have played a crucial role in the geochemical cycle of the Earth's interior. Mineral solubility and speciation in aqueous fluids at high pressure (P) and temperature (T) conditions are the basis for characterizing the chemical property of subduction-zone aqueous fluids. This thesis focuses on in-situ observations and Raman spectroscopic analyses in mineral–aqueous fluid systems under high P – T conditions using a hydrothermal diamond anvil cell (HDAC). Two of the four chapters in the thesis (Chapters 2 and 3) present the experimental studies on the solubility behaviors of (1) silica (SiO_2) as a major constituent of subduction-zone lithologies and fluids and (2) rutile (TiO_2) as a host mineral of high field strength elements. Understanding these key rock components in aqueous fluids at high P – T conditions provides insights into the metal cycles in the subduction-zone system.

The Chapter 2 reveals silica solubility and speciation in alkaline Na_2CO_3 and NaOH solutions at high P – T conditions. With an aim at understanding the interactions between alkaline fluids and silicate rocks in subducting slabs, I made in-situ observations of the quartz dissolution in the HDAC up to 750 °C and 1.5 GPa. The results underscored the enhancing effects of 0.5 and 1.5 m Na_2CO_3 and 0.5 m NaOH solutions on silica solubility. Comparison of the silica solubility in Na_2CO_3 solutions with thermodynamic calculations suggested an insufficiency of the available speciation modeling to explain the observed high solubilities. The solubility measurements and simultaneous in-situ Raman spectroscopy allowed the identification of the silica oligomers contributing to the solubilities. The prevalent presence of deprotonated monomers in the experimental solutions suggests the presence of deprotonated silica oligomers or sodium-involving silica oligomers. These contexts indicate that the silicates dissolved in alkaline subduction-zone fluids are partly present as anionic silica species and silica oligomers, which may act as complexing agents for mobilizing metals. The Chapter 3 demonstrates rutile solubility in various sodium salt solutions (0.5 and 1.0 m Na_2CO_3 , 1.0 m NaHCO_3 , 1.0 m Na_2SO_4 , 1.0 m NaF , and 3.0 m NaCl) up to 1012 °C and 1.7 GPa. I applied the same HDAC approach to ascertain

the role of potential ligands for titanium complexes in subduction-zone fluids. The addition of Na_2CO_3 , NaHCO_3 , Na_2SO_4 , and NaF to H_2O increased the solubilities of rutile by an order of magnitude compared to those in pure H_2O previously determined by a piston-cylinder method. The observed high solubilities can be explained by the formation of Ti hydrolysis species and/or Ti complexes with sodium or the anionic ligands. These dissolution mechanisms contribute to the interpretations of some natural observations of extraordinary Ti mobility in alkaline carbonic fluids within exhumed high to ultrahigh pressure slabs in orogens. In addition, the speciation of Ti might control whether the dissolved Ti is trapped by precipitation processes in the slab–mantle interfaces, or transported by subduction-zone aqueous fluids across the interfaces.

These two experimental approaches can lead to a better understanding of the efficiency of the elemental transport via aqueous fluids from subducting slab to the overlying crust and upper mantle, which strongly depends on alkalinity or availability of complexing agents in subduction-zone fluids. The obtained results might further expand our understanding of subsolidus fluid-mediated processes including but not limited to terrestrial and extraterrestrial environments.