

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

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## 論 文 要 旨

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 ( $\text{SiO}_2$ ) as a major constituent of subduction-zone lithologies and fluids and (2) rutile ( $\text{TiO}_2$ ) 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  $\text{Na}_2\text{CO}_3$  and  $\text{NaOH}$  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  $m$   $\text{Na}_2\text{CO}_3$  and 0.5  $m$   $\text{NaOH}$  solutions on silica solubility. Comparison of the silica solubility in  $\text{Na}_2\text{CO}_3$  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  $m$   $\text{Na}_2\text{CO}_3$ , 1.0  $m$   $\text{NaHCO}_3$ , 1.0  $m$   $\text{Na}_2\text{SO}_4$ , 1.0  $m$   $\text{NaF}$ , and 3.0  $m$   $\text{NaCl}$ ) 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  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{NaF}$  to  $\text{H}_2\text{O}$  increased the solubilities of rutile by an order of magnitude compared to those in pure  $\text{H}_2\text{O}$  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.

## 別 紙

### 論文審査の結果の要旨

本論文は、地球内部の地球化学的循環において重要な役割を担うプレート沈み込み帯の水流体の化学的特性を明らかにするため、水熱ダイヤモンドアンビルセル (HDAC) を用いたその場観察及びラマン分光法を組み合わせた高温高压実験により、深部地殻に相当する温度圧力条件下で  $\text{SiO}_2$  (石英) と  $\text{TiO}_2$  (ルチル) の水流体への溶解度と溶存化学種を調べた。著者は、地球内部に向かって沈み込んでゆく地殻物質と化学的に平衡状態にある流体が、炭素や硫黄などを含む多成分系でアルカリ性の特性をもつことに着目し、複雑な組成を持つ流体への石英とルチルの溶解挙動の解明を試みた。HDAC によって模擬した高温高压環境下で  $\text{Na}_2\text{CO}_3$  及び  $\text{NaOH}$  水溶液中の石英溶解度測定とラマン分光法による流体中の珪酸塩構造測定を系統的に行った結果、アルカリ性水溶液に対する石英の溶解度は高温高压条件下でも純粋な水への溶解度よりも高く、単純な溶存化学種を考慮した熱力学モデルでは再現できないことが明らかとなった。また、脱プロトン化した珪酸塩重合種や  $\text{Na}$  イオンが関与した珪酸塩重合種がその高い溶解度に寄与する可能性をラマン分光学的観点からはじめて言及した。これらの結果は、流体中の珪酸塩溶解度と溶存形態の実体だけでなく、沈み込み帯の金属元素輸送に関して定性的な理解を深めた。研究成果は筆頭著者論文として国際誌に掲載受理された。さらに本論文は、高温高压条件下における多様な  $\text{Na}$  塩水溶液 ( $\text{Na}_2\text{CO}_3$ 、 $\text{NaHCO}_3$ 、 $\text{Na}_2\text{SO}_4$ 、 $\text{NaF}$  水溶液) へのルチルの溶解度を調べた。それにより、純水と比べて  $\text{Na}$  塩水溶液に対するルチル溶解度が最大で一桁増加することを明らかにした。この知見は沈み込み帯深部における流体を媒介した  $\text{Ti}$  の移動が流体の  $\text{pH}$  または錯体を形成する配位子の存在度により制御されることを示し、天然の高压変成岩に観察される特異な  $\text{Ti}$  移動濃集プロセス対して新解釈を与える。本論文は上述の HDAC を用いた研究に加え、副課題としてカリフォルニア産ひすい輝石岩についての研究を含む。CL 分光法を用いた岩石学的研究と、多角的な組織記載に先端的な局所  $\text{Li}$  同位体比・微量元素分析を応用した地球化学的研究に取り組み、筆頭著者として国際誌 2 編に成果発表した。

以上の研究成果及び業績は、自立して研究活動を行うに必要な高度の研究能力と学識を有することを示している。したがって、提出の博士論文を博士 (理学) の学位論文として合格と認める。