Does subducted ammonium hydrogenate the mantle?

The University of St. Andrews
In partnership with Durham University, and the Universities of Glasgow, Edinburgh, and Oxford (Ref. IAP_15_07)

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Key Words

Overview

Simplified rationale:

The importance of the global hydrogen-nitrogen cycle cannot be understated. These elements are fundamental to the evolution of planet Earth and the life it supports, including but not limited to, the formation and evolution of the atmosphere and hydrosphere. Therefore, understanding the Earth’s coupled hydrogen - nitrogen cycle is central to unravelling what made (and continues to make) Earth a habitable planet capable of supporting life over long timescales (billions of years).

The abundance of hydrogen inside Earth has a dramatic effect on life at the surface: it buffers the amount of liquid water present in the oceans, and therefore the composition of the atmosphere. We aim to better understand the hydrogen storage capacity of the Earth (Fig.1) by determining the importance of ammonium as a reservoir of hydrogen. This information will provide the fundamental knowledge required to model and re-evaluate the hydrogen budget of entire planets, and more specifically, enhance our understanding of the volatile content of the Earth.

The hydrogen budget of the Earth’s surface and interior are in a constant state of flux. Plate tectonics transfers hydrogen from Earth’s surface to the interior, and magmatism provides the mechanism for returning hydrogen to the surface. The focus on this PhD is to address the flux of hydrogen transported as ammonium.

Figure 1. The main hydrogen stores in the silicate mantle and metallic outer core: (a) the storage capacities of hydrogen as H₂O in the mantle (data compiled in Hirschmann, 2006), and (b) the proposed mineral phases capable of storing hydrogen as ammonium (dependent upon the exchange equilibrium between NH₄ and K).
Introduction:

In cosmochemical terms, there is a missing nitrogen conundrum. By summing up the volatile abundances for the bulk silicate Earth and comparing those to chondritic meteorites it is evident that nitrogen is the most depleted of the volatile elements (Fig. 2; Marty, 2012). The missing nitrogen is either stored in the mantle, core, or both (Halliday, 2013). Ergo, by determining the abundance of nitrogen stored in either the core or mantle, we can determine the other. The question we will answer is: what is the likely abundance of ammonium in the mantle, and how does this alter the conceptual understanding of Earth’s total H-storage capacity (Fig. 1a)?

Existing geochemical (Busigny et al., 2011), cosmochemical (Marty, 2012), and experimental (Watenpaul et al., 2009) data require a deep nitrogen reservoir within the mantle and core (Halliday, 2013). Without constraints on the abundance of either, one cannot constrain the other.

The student will address both the ‘missing nitrogen conundrum’ and calculate the actual storage capacity of hydrogen in the mantle by determining the exchange coefficient for NH₄⁺ and K⁺ under mantle conditions. This will enable us to calculate the storage capacity of hydrogen and nitrogen in the mantle, and model the flux (quantitatively).

Primary Objectives:

The specific scientific objectives for this Ph.D project are as follows:

1. Constraining the major petrologic controls on the relative partitioning behaviour of ammonium and potassium

2. Determining what the overall ‘storage capacity’ of hydrogen as ammonium in the mantle

Approach:

[1] Experimental Approach

To determine if ammonium is a significant re-hydrogenation agent and hydrogen reservoir in the mantle requires an experimental programme.

Sample Synthesis. The relative partitioning behaviour of ammonium and potassium during partial melting and fluid/melt-rock interaction will be investigated. A piston cylinder press (1 - 4 GPa) at the Univ. St Andrews and a multi-anvil press (3 - 20 GPa) at the Univ. Edinburgh will be used for mineral synthesis. The collective pressure-temperature range for the experiments is from 1-20 GPa across a temperature range to represent hot and cold subduction geotherms. The aim is to simulate conditions of the lower crust, upper mantle, and transition zone with a bias to subduction-induced conditions. The minimum-maximum pressures and temperatures for the experiments will be constrained by the stabilities of the mineral phases. The minerals of interest therefore evolve with increasing P-T, in short:

1. During the early stages of subduction (1-4 GPa), the K-bearing phases are mica-dominated

2. At around 5 GPa (ca. 150 km depth), K-clinopyroxene is introduced to the mantle potassium budget, and alongside phlogopite is the main potassium host in the majority of the upper mantle

3. With continuing subduction the slab exits the stability field of K-clinopyroxene and majorite garnet becomes stable (circa 15 GPa). At this stage the dominant host for potassium transfers

![Figure 1. Abundance of volatile elements in the bulk silicate Earth relative to carbonaceous chondrites (modified from Marty, 2012).](image-url)
[2] **Analytical Approach**

**Sample characterization.** Major and minor element abundances will be determined between the K-phases and melts using electron microprobe and SIMS (Univ. St Andrews and Edinburgh, respectively) after lattice bound ammonium has been identified using FTIR spectroscopy (Univ. St Andrews). A systematic approach will be performed to evaluate the effects of pressure, temperature, and bulk composition on the relative partitioning behaviour of ammonium and potassium in the stability fields of the phases.

**Methodology**

The student will utilise several analytical methodologies at the host and partner institutions to extract data from natural samples, listed below:

- Electron microprobe (St Andrews)
- Infrared spectroscopy (St Andrews)
- SIMS (Edinburgh)
- Laser-ablation gas-sourced mass spectrometry (SUERC)
- Piston Cylinder Experiments (St Andrews)
- Multi-Anvil Experiments (Edinburgh)

**Timeline**

**Year 1:** Initial training in microanalysis and experimental petrology. The student will attend the Bristol micro-analysis workshop (UK) and the BGI experimental petrology workshop (Germany). Standardisation protocols will be established and high-pressure experiments will commence at St. Andrews (lower crustal & upper mantle conditions).

**Year 2:** Continue the high-pressure experiments at St. Andrews, begin the high-pressure experimental programme at Edinburgh (upper mantle & transition zone conditions). Present results at international meeting (Goldschmidt & AGU Fall meeting).

**Year 3.5:** Write thesis.

**Training & Skills**

This IAPETUS DTP project will provide training in petrology and stable isotope geochemistry, and the data generated will be focused on explaining the Earth’s total volatile budget (biased towards nitrogen and hydrogen).

The student will also attend training workshops on micro-analysis (at Bristol University, UK) and experimental petrology (Bayreuth University, Germany).

The focus on petrological characterization of minerals, advanced analytical geochemistry, and high-pressure material synthesis will provide the student a skill-set to competitively acquire postdoctoral research positions, or to transition from an academic to industrial career in Material Sciences upon completion of their Ph.D degree.

**References & Further Reading**


**Further Information**

For further information please contact Dr. Sami Mikhail (sm342@st-andrews.ac.uk).