

## The oxidation state of iron in the lower mantle

D.J. FROST AND F. LANGENHORST

Bayerisches Geoinstitut, Universität Bayreuth, Bayreuth, Germany. (Dan.Frost@uni-bayreuth.de, Falko.Langenhorst@uni-bayreuth.de)

Determining the redox state of the lower mantle is important because it will influence processes, such as chemical diffusion, electrical conductivity and volatile speciation. Using a multianvil apparatus we have measured the partitioning of  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Mg}^{2+}$  between magnesiowüstite and magnesium silicate perovskite in both  $\text{Al}_2\text{O}_3$ -bearing and  $\text{Al}_2\text{O}_3$ -free systems under variable redox conditions. In the  $\text{Al}_2\text{O}_3$ -bearing system perovskite  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios are as high as 80%, which is over 3 times greater than for  $\text{Al}_2\text{O}_3$ -free perovskite. The variation in the  $\text{Fe}^{3+}$  solubility with the  $\text{Al}^{3+}$  content of perovskite is non-linear.

If, as some previous studies have indicated, the influence of Al on the  $\text{Fe}^{3+}$  content of perovskite is indeed independent of the oxygen fugacity, then for a typical mantle  $\text{Al}_2\text{O}_3$  content of 4 wt %, silicate perovskite in the lower mantle would have an  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio of approximately 70% and a bulk peridotite would have an  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio of 50 %. Upper mantle xenoliths suggest an average mantle  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio no higher than 3%, however, which would infer one of two possible scenarios for the lower mantle. Either the lower mantle contains more  $\text{Fe}^{3+}$  i.e. more oxygen, than the upper mantle or lower mantle perovskite must sequester oxygen by reducing vapour phases and through the precipitation of metallic Fe. As the vapour content of the mantle can account for only a minor proportion of the required oxygen the only feasible mechanism would be the disproportionation of FeO to produce approximately 1 wt. % metallic Fe. This metallic phase would also be supplemented by other siderophile elements. We have made a number of experiments in the presence of metallic iron in order to test this possibility. We also compare these results with analyses of inclusions found in diamonds which are considered to have formed in the lower mantle.

## REE pattern of carbonaceous part of coals: a new proxy for the original plants of coals

FENGFU FU<sup>1</sup>, TASUKU AKAGI<sup>2</sup>, YUICHIRO SUZUKI<sup>3</sup> AND SADAYO YABUKI<sup>4</sup>

<sup>1</sup>Department of Environmental Sciences, JAERI, Tokai, Ibaraki 319-1195, Japan (fengfu@acl.tokai.jaeri.go.jp)

<sup>2</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology, Fuchu, Tokyo, Japan (akagi@cc.tuat.ac.jp)

<sup>3</sup>Institute for Geo-Resources and Environment, AIST, Tsukuba, Japan

<sup>4</sup>Division of Surface Characterization, RIKEN, Wako, Saitama 351-0198, Japan

### Introduction

It is generally thought that most coals are originated from trees and peat, and some of them are from algae. However, the inference of the original plants is sometimes a difficult problem. The study on REEs in coals is expected to provide us with some knowledge about the original plants of coal.

### Experiment

Coal samples of the Taiheiyō coal mine, the Ashibetsu, the Ambalut coal mine, and boghead coal were collected in this study. Each sample was divided into carbonaceous part and mineral part by treating ashed coal with 10 % acetic acid solution. REEs in each part were determined with ICP-MS.

### Discussion of results

The chondrite-normalized REE patterns of the carbonaceous part of all the coals can be classified into three types. The Ashibetsu coals, the Taiheiyō coals and some of the Ambalut coals are type I, which is featured with a medium slope and no depletion in Ce (no Ce anomaly). The others of the Ambalut coals are classified into type II, which is characterized with a steeper slope (greater LREE/HREE ratio) than type I and a Ce negative anomaly. The boghead coal was classified into type III, which is featured with a smaller slope than type I and a Ce negative anomaly. Compare with the extents of the Ce anomaly and slope of the pattern of plants we have surveyed so far, we can infer that coals classified into the type I, type II, and type III are originated from peat vegetation, trees and seaweed, respectively. This correspondence is consistent with the result of maceral study.

### Conclusions

The REE pattern of the carbonaceous part in coals is shown to be a good proxy for the original plants to be coalified.

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