

The geochemistry of Ni isotopes in mafic-ultramafic layered complexes

D.S. SERGEEV¹, A.S. SERGEEV², E.M. PRASOLOV^{2,3},
I.N. KAPITONOV³ AND S.A. SERGEEV^{2,3}

¹University of Neuchatel, Institute of Geology, Switzerland;
(dmitry.sergeev@unine.ch)

²Saint-Petersburg State University, 7/9 Universitetskaya em.,
199034 St.-Petersburg, Russia

³Centre of Isotopic Research, VSEGEI, 74 Sredny pr.,
St.-Petersburg, Russia; (sergey_sergeev@vsegei.ru)

Introduction

For better understanding the natural processes involved in the formation of Ni ore deposits in igneous layered complexes, we analyzed Ni isotopes in a section through the 2.45 Ga Burakovsky layered mafic-ultramafic massif (NW Baltic Shield, Russia). In order to constrain the mechanisms of Ni isotope fractionation, we also analysed Ni isotopes in samples that have undergone Ni-enriching by the Mond process, where synthesis gas (95-97% CO and H) is used for highly effective Ni extraction involving metal-carbonyl formation.

Analyses were made on whole-rock (WR) samples and on separated pyroxenes and Ni-rich sulphide minerals with a Neptune MC-HR-ICP-MS. The measuring precision achieved for δNi was at $\pm 0.1\%$ with a maximum observed fractionation value for $\delta^{62}\text{Ni}/^{60}\text{Ni}$ of 5‰.

Results

1) WR samples from the section through the Burakovsky Massif (BM) (from -700 to -50m) show a clear fractionation trend of enrichment of light Ni isotopes from the base towards the roof of the massif (change of $\delta^{62}\text{Ni}/^{60}\text{Ni}$ of +0.3‰ at the base, towards -1.5‰ at the top).

2) Ni-rich sulphide secondary minerals, which are forming the upper layer of the intrusion, have the lightest measured Ni isotope composition in the natural samples, in particular those which are associated with carbon minerals ($\delta^{62}\text{Ni}/^{60}\text{Ni} = -2\%$).

3) The Ni isotope ratios in pyroxenes changes independently of their position in the section. This may indicate the importance of a secondary, low temperature process.

4) Materials from the technological process of metallic nickel production show the most intensive $^{62}\text{Ni}/^{60}\text{Ni}$ and $^{61}\text{Ni}/^{60}\text{Ni}$ fractionation ($\delta^{62}\text{Ni}/^{60}\text{Ni}$ from +0.5 to -4.5‰). Lighter isotopes accumulate in the chamber's top, where the gas phases condense.

5) Gas analyses from the BM WR samples show up to 41.5 vol% of ($\text{N}_2 + \text{CO}$) component.

Interpretation

The observed trends of Ni isotopic fractionation in the BM rock, similar to those observed in the technological Mond process, as well as the presence of trapped ($\text{N}_2 + \text{CO}$) gasses, suggest a model of natural kinetic Ni fractionation involving reducing gasses and natural metal-carbonyl formation. Such gasses may either have a juvenile origin or may be formed from heating (intrusion contact, metamorphism) and water vaporization of carbon-bearing geological units.

Development of a mosaic-like micro-pattern during Mg-calcite crystal growth

INGO SETHMANN

Institut für Mineralogie, Universität Münster, Corrensstr. 24,
D-48149 Münster, Germany. (isethma@uni-muenster.de)

In natural calcium carbonate precipitation systems, Mg^{2+} ions play a major role due to their inhibiting effect on calcite growth and the formation of $\text{CaCO}_3\text{-MgCO}_3$ solid solutions, resulting in the modification of precipitation kinetics and rates, thermodynamic stability of the precipitate, as well as in changes of crystal morphology. Marine sedimentary and biomineralized Mg-calcite crystals have been reported to contain up to about 20 mole% MgCO_3 , although such high-Mg-calcite crystals are considered to be metastable under seawater-like conditions. These natural Mg-calcite crystals usually show micro-morphologies different from pure calcite crystals.

To explore deeper into the conditions of high-Mg-calcite formation, Mg-calcite growth under different solution conditions has been directly observed using atomic force microscopy. Within a certain range of solution conditions, dependent on the Mg/Ca ratio in solution, on the saturation state, as well as on the presence of other ions in solution, an intriguing observation of crystal restructuring has been made: After fast crystal growth by step advancement as well as by two-dimensional nucleation and spreading of monolayer-islands on calcite cleavage faces, straight ridges of sub-nanometre height appeared at the crystal surface. These ridges do not grow on the crystal surface, but they pop up by bulging of the newly precipitated crystal layers. Ridge formation starts at one point and usually proceeds in one direction until they connect to another ridge or stop at a major crystal defect. Ridges occur in three crystallographically defined directions, which probably correspond to the equivalent planes of the prismatic {11 2 0} form. Through progressive development of new ridges, the growing crystal becomes subdivided into mosaic blocks that can be reduced down to a few hundreds of nanometres in diameter. When advancing steps stop at ridges, they pile up to form multilayer steps that separate the mosaic blocks from each other, which may finally lead to crystal growth as aligned fibres.

EDX analyses yielded a bulk content of about 8-10 mole% MgCO_3 in the mosaic calcite, which should increase its solubility in water. However, dissolution of a mosaic takes place preferentially along the ridges, which may suggest a shift of the bulk strain and possibly exsolution-like dislocation of magnesium ions towards preferential crystallographic planes, where the accumulated strain gives rise to the ridges.

The described mechanism of crystal restructuring may have implications for the formation kinetics of $\text{CaCO}_3\text{-MgCO}_3$ solid solutions, and it may play a role in the formation of crystal ultrastructures, such as in biominerals.