

LA-UR-01-4382

Approved for public release;
distribution is unlimited.

Title:

SERPENTINITES USED FOR CARBON DIOXIDE SEQUSTRATION: A POSSIBLE ECONOMIC SOURCE FOR PGE

Author(s):

Katherine Anne Porter

Submitted to:

<http://lib-www.lanl.gov/la-pubs/00796291.pdf>

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the U.S. Department of Energy under contract W-7405-ENG-36. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

SERPENTINITES USED FOR CARBON DIOXIDE SEQUESTRATION: A POSSIBLE ECONOMIC SOURCE FOR PGE

Katherine Anne Porter
EES-6
IGPP, MS C305
Los Alamos National Laboratory
Los Alamos NM 87545
ph 505 665 2863
fax 505 665 3107
kporter@lanl.gov

ABSTRACT

The platinum-group elements (PGE: Ru, Rh, Pd, Os, Ir, Pt) are among the most valuable metals in the world. Their myriad uses in electronics, jewelry, catalysis, and the automotive industry have increased PGE demand several fold in the last few decades, but the past few years have seen PGE supply largely unable to keep up with the increasing demand. Although the PGE are found in many types of rock bodies, in most cases they are present in such low concentrations that it is not economically feasible to extract them. The few economically mineable deposits generally fall into two categories: layered ultramafic intrusive deposits, such as the Bushveld Complex in South Africa, which contain PGE-bearing ore veins; and copper/nickel-bearing veins, such as the Noril'sk-Talnakh District in Russia, in which the PGE are extracted as a byproduct of Cu/Ni mining. Only one economic PGE deposit exists in the United States (the Stillwater Complex in Montana), and it is small compared to the Russian and South African deposits (which supply most of the world's PGE needs).

The recent interest in the use of serpentinites and ultramafic rocks as possible reservoirs for carbon dioxide sequestration has opened the door to another possible economic source for the PGE. Theoretically, the magnesium silicates in the ultramafic rocks and serpentinites can be reacted with carbon dioxide (either from the air or as a waste stream from a fossil fuel plant) to produce thermodynamically and geologically stable magnesium carbonates, which can be easily disposed of. The deposits being investigated for this process are located throughout the world; there are several in the U.S. alone. The PGE concentrations in these deposits are fairly low, and by themselves the deposits are not economically feasible sources for the PGE. However, part of the proposed carbonation process requires the crushing and magnetic separation of the rocks; the non-magnetic fraction is used for carbonation, while the magnetic fraction is treated to extract iron and other metals. Since most PGE-bearing minerals in serpentinites and ultramafic rocks are magnetic or are associated with magnetic minerals, the magnetic separation of the powder could serve to essentially concentrate the PGE from the rock bodies. Once the PGE-bearing minerals have been separated and concentrated, the PGE may be at economically extractable levels.

The primary focus of this research is the investigation of the PGE concentrations in the serpentinites and ultramafic rocks that may be utilized in the carbonation process. The magnetic fraction from a representative serpentinite body will be analyzed for PGE to determine whether or not these rocks may be economic sources of the PGE.

INTRODUCTION

Mineral sequestration of CO₂ is a promising method for removing CO₂ from the atmosphere. In this process, CO₂ – whether as a waste stream from a power plant or concentrated from the air – is reacted with magnesium silicates such as olivine (Mg₂SiO₄) or serpentine (Mg₃Si₂O₅(OH)₄) to produce magnesite (magnesium carbonate, MgCO₃) and sand (SiO₂; the reaction with serpentine also produces water). Magnesite and sand are thermodynamically and geologically stable at the surface of the Earth; in fact, the reaction of CO₂ with magnesium silicates is a natural weathering reaction that occurs at the surface. The mineral carbonation process simply speeds up the weathering reaction to remove CO₂ from the air more rapidly [1].

The rocks that could be used for mineral carbonation abundant and easily accessible throughout the world [2]. The rock bodies that would be the primary sources for serpentine and olivine for this process are generally classified as layered ultramafic or intrusive bodies; there are several large bodies in the United States and Puerto Rico alone [3].

Layered ultramafic bodies have been extensively studied, since the world's major supplies of platinum-group elements (PGE) are largely found in such formations [4]. For example, the two main sources of PGE for most of the world are the Bushveld Layered Intrusion in South Africa and the Noril'sk Layered Intrusion in Russia [4]. There are several smaller bodies that contain economic PGE concentrations in North America and Europe, but they are much smaller in output and potential than the South African and Russian deposits. Most ultramafic layered bodies are enriched in PGE relative to other crustal rocks; however, in general the PGE are present in sufficiently low concentrations that it is not economically practical to mine them.

Although most layered ultramafic bodies do not contain sufficient PGE to make their mining economic, it is possible that the PGE in these bodies would become economically mineable if the rocks were used in the CO₂ sequestration process. This process involves the removal, grinding, and magnetic separation of the serpentines; the nonmagnetic fraction is processed for carbonation, and the magnetic fraction is simply a waste stream. However, many PGE-bearing phases occur as inclusions in magnetic minerals [5], so it is possible that any PGE in the serpentines would be concentrated in the magnetic "waste" fraction. If the PGE are present in this magnetic fraction in sufficient concentrations, the waste fraction could be sold as a PGE ore to a refining company. Since the magnetic fraction contains high concentrations of chromium and other heavy metals, which are regulated by the Environmental Protection Agency and are expensive to dispose of, sale of the ore would remove the disposal cost associated with the heavy metals and reduce the overall process cost. Sale of the waste stream as a PGE ore would most likely yield a higher return than its sale as an iron or chromium ore, provided that the PGE are present in sufficient concentration. The primary goal of this

research is to determine whether or not a magnetic waste stream from a serpentinite might contain economic levels of PGE.

PROCEDURE

A magnetic separate from sample UM9801 (a serpentinite from Clearlake, California) was subjected to 9 passes of a hand magnet; the resulting highly magnetic fraction was cured in epoxy on a one inch round glass slide. The epoxy containing the sample was polished to less than 0.5 mm thickness. The slide was examined for bulk chemistry and mineral morphology using a Tracor ADEM Scanning Electron Microscope (SEM). Both backscattered and secondary electron images were collected. In addition, x-ray diffraction (XRD) and electron microprobe (EMPA) data were collected on the sample.

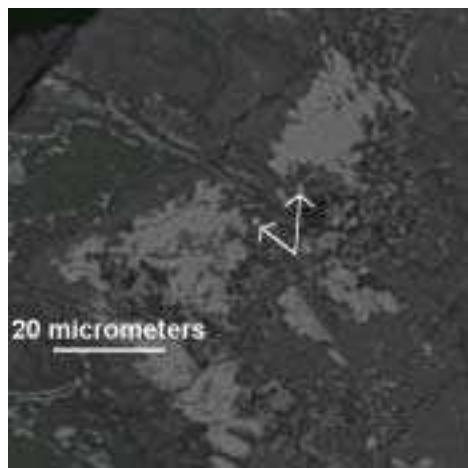


Figure 1. Nickel-iron sulfide (arrows) associated with magnetite (bright) and chlorite (dark).

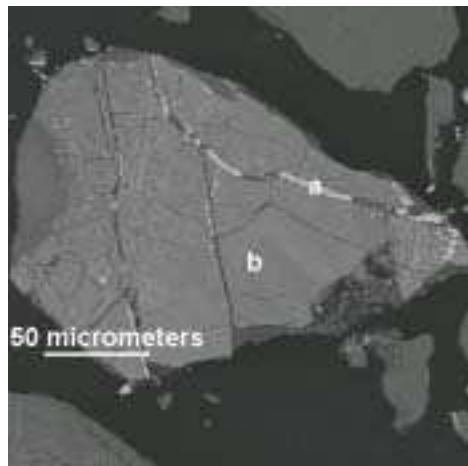


Figure 2. Well-defined magnetite veins (a) in grain containing finely disseminated chromite and chlorite (b). Most chromite observed was finely crystalline and not well delineated.

RESULTS

XRD data showed that the sample contains primarily magnetite, maghemite, and clinochlore. Minor amounts of chromite and chromian clinochlore are probably also present, but the similarity of their XRD patterns to those of magnetite and clinochlore

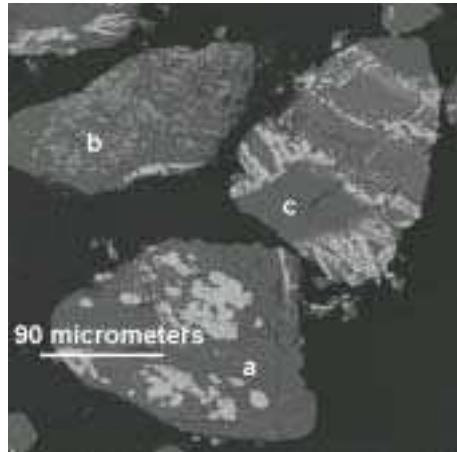


Figure 3. Major iron/chromium/silicate morphologies: a) euhedral magnetite grains (bright) in serpentine (dark) matrix; b) feathery magnetite growths in serpentine matrix; c) chromian magnetite veins (brightest) in grain containing finely disseminated chromite (medium grey) and chlorite (dark grey).

lead to difficulty in identification. The sample was examined for platinum-group minerals (PGM), Au, Fe, Cr, Ni, and S using SEM and EMPA. No PGM or Au grains were found. Few nickel- or sulfur-bearing phases were observed; the few nickel sulfide mineral grains that were found were extremely small and associated with iron-rich phases (figure 1). Chromium and iron were found to be present in large quantities, with iron-rich phases showing more well defined morphology than chromium-rich phases (figure 2). Three primary Fe-bearing phase morphologies were observed (figure 3): 1) well-formed euhedral magnetite crystals enclosed in a magnesium-iron silicate; 2) feather-like, microcrystalline magnetite enclosed in a magnesium-iron silicate; and 3) vein- or crack-filling Fe-rich phases associated with Cr-bearing silicate phases. Chromium occurred primarily as a finely disseminated Cr-rich phase (probably chromite) in Mg/Al silicate (probably clinochlore), although many of the Fe-rich vein-filling phases contained minor amounts of chromium.

DISCUSSION & CONCLUSIONS

No discrete PGM or Au grains were observed in the magnetic fraction examined, but it may contain PGE nonetheless. Whole-rock analyses of chromitite (rock containing 20-50% chromite) veins and bodies associated with other layered ultramafic bodies have shown appreciable PGE concentrations, even when no PGM were observable in polished section [6]. The chromitites examined in other studies occurred as both primary mineral phases and as hydrothermal alteration products [5, 7-12]. One study indicated that

primary chromites were more enriched in PGE than were secondary chromites [7]. However, in most layered ultramafic bodies, chromitite veins (either primary or secondary) are considerably enriched in PGE relative to the host rock [10-12]. It is likely, therefore, that the sample analyzed in this study does contain at least a small concentration of PGE, even though no PGM were observed in the polished section. Additional analytical work on this sample (mass spectrometry and x-ray fluorescence) is currently in progress; the results of these analyses will help to confirm or deny the presence of PGE in this sample.

ACKNOWLEDGEMENTS

I wish to thank Peg Snow for her assistance in sample preparation, instrumentation set-up and troubleshooting, and data analysis; Steve Chipera, Dale Counce, and Emily Kluk for performing XRD, ICP-MS, and XRF analyses; George Guthrie, for his guidance; and the Hertz Foundation, for allowing me the opportunity to study at LANL.

REFERENCES

1. Lackner, K.S., D.P. Butt, C.H. Wendt, F. Goff, & G. Guthrie, 1997. Carbon dioxide disposal in mineral form: keeping coal competitive. Los Alamos National Laboratory report LAUR-97-2097 (abbreviated).
2. Ziock, H-J., K.S. Lackner, & D.P. Harrison, 2001. Zero emission coal power, a new concept. Los Alamos National Laboratory report LAUR-01-2214.
3. Goff, F., G. Guthrie, B. Lipin, M. Fite, S. Chipera, D. Counce, E. Kluk, & H. Ziock, 2000. Evaluation of ultramafic deposits in the eastern United States and Puerto Rico as source of magnesium for carbon dioxide sequestration. Los Alamos National Laboratory report LA-13694-MS.
4. Fogg, C.T., & J.L. Cornellisson, 1993. Availability of platinum and platinum-group metals. Bureau of Mines Information Circular 9338.
5. St. Louis, R.M., B.E. Nesbitt, & R.D. Morton, 1986. Geochemistry of platinum-group elements in the Tulameen ultramafic complex, Southern British Columbia. *Economic Geology* 81: 961-973.
6. Franklin, B.J., B. Marshall, I.T. Graham, & J. McAndrew, 1992. Remobilization of PGE in podiform chromitite in the Coolac Serpentinite Belt, Southeastern Australia. *Australian Journal of Earth Sciences* 39: 365-371.
7. Angeli, N., M.E. Fleet, Y. Thibault, & M.A.F. Candia, 2001. Metamorphism and PGE-Au content of chromitite from the Ipanema mafic/ultramafic Complex, Minas Gerais, Brazil. *Mineralogy and Petrology* 71: 173-194.
8. Mogessie, A., E.F. Stumpf, & P.W. Weiblen, 1991. The role of fluids in the formation of platinum-group minerals, Duluth Complex, Minnesota: Mineralogic, textural, and chemical evidence. *Economic Geology* 86: 1506-1518.
9. Vatin-Perignon, N., J. Amosse, L. Radelli, F. Keller, & T. Castro Leyva, 2000. Platinum group element behaviour and thermochemical constraints in the ultrabasic-basic complex of the Vizcaino Peninsula, Baja California Sur, Mexico. *Lithos* 53:59-80.

10. Zhou, M-F., M. Sun, R.R. Keays, & R.W. Kerrich, 1998. Controls on platinum-group elemental distributions of podiform chromitites: A case study of high-Cr and high-Al chromitites from Chinese orogenic belts. *Geochimica et Cosmochimica Acta* 62: 677-688.
11. Economou-Eliopoulos, M., & I. Vacondios, 1995. Geochemistry of chromitites and host rocks from the Pindos ophiolite complex, northwestern Greece. *Chemical Geology* 122: 99-108.
12. Bacuta, G.C., R.W. Kay, A.K. Gibbs, & B.R. Lipin, 1990. Platinum-group element abundance and distribution in chromite deposits of the Acoje Block, Zambales Ophiolite Complex, Philippines. *Journal of Geochemical Exploration* 37: 113-145.