152. Nickel Content of Olivines

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Introduction. Nickel is one of the most important trace elements which are sensitively influenced by the process of magmatic differentiation, and its content in various rock-forming minerals shows regular decrease with the advance of fractional crystallization. In order to study the behavior of nickel during the fractional crystallization we have determined the nickel content of olivines of different origin from various localities. Most of the samples studied were collected by Yagi, except the pallasites and some specimens in the collection of the Department of Geology and Mineralogy, Hokkaido University. Pure samples were separated from the specimens by Yagi, and Yamamoto. The Fo content was determined optically by Yagi, and nickel was determined spectrophotometrically by Nishimura and Yamamoto.

Mineralogical Description on the Samples. The olivines studied here can be grouped into the following four categories according to their origin.

(A) Olivine from olivine nodules in alkalic olivine basalts. No. 100: Locality—Peridot Cove, Arizona, U.S.A. Aggregates of grass-green olivine crystals enclosed in alkalic basalt.

No. 2716: Locality—Tetsugen, Kogendo, Korea (Hokkaido University collection). Aggregates of yellowish green olivine crystals in basaltic rock.

No. 604B and No. 604C: Locality—Hale Pohaku, Mauna Kea, Hawaii, U.S.A. Both samples are aggregates of pale green olivine crystals enclosed in compact trachybasalt from a parasitic cone of Mauna Kea. No. 701: Locality—The 1801-flow of Hualalai volcano, Hawaii, U.S.A. Aggregates of pale green olivine in rather coarse-grained 1801-flow of Hualalai volcano.

(B) Olivine from dunites.

H-A, H-B, H-C, and H-D: Locality—Horoman ultramafic complex,

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Horoman, Hokkaido, Japan. All the samples were collected from various parts within the Horoman ultramafic intrusive complex. The host rocks are rather coarse-grained, pale green dunite with sporadic chromite crystals.

(C) Olivine phenocryst in olivine tholeiites.

No. 401: Locality—Halemaumau, Kilauea, Hawaii, U.S.A. Large phenocrysts in the pre-historic olivine tholeiite of Kilauea.

No. 305: Locality—Kilauea Iki, Kilauea, Hawaii, U.S.A. Large phenocrysts in the olivine tholeiite flowed out by the 1959-activity of Kilauea Iki.

No. 36 and No. 37: Locality—Stapi, Iceland. Olivine sands on the beach, derived from the disintegration of olivine tholeiite from Stapafel volcano. The grains are fresh, and yellow in color.

No. 243: Locality—Miyake-jima volcano, Japan (Hokkaido University collection). Olivine sands on the beach derived from the disintegration of pre-historic lava flows of the olivine tholeiite of Miyake-jima volcano. The olivine is fresh and yellow in color.

No. 2809: Locality—Shimushiru (Simushir) Island, Kurile Islands, U.S.S.R. (Hokkaido University collection). Olivine sands on the beach derived from the disintegration of olivine tholeiite of a volcano in Shimushiru Island. The olivine is fresh and yellow.

No. 2001: Locality—Crater-rim of Kuttara caldera, Hokkaido, Japan. Olivine crystals enclosed in large anorthite phenocrysts or xenocrysts in olivine pyroxene andesitic basalt of Kuttara caldera. The olivine is large and fresh, deep yellow in color.

(D) Olivine from olivine nodules in pallasites (stony-iron meteorites).

Zaisho: Pallasite, Kochi Prefecture, Japan, given by the National Science Museum, Tokyo.

Brenham: Pallasite, Kansas, U.S.A., given by Dr. Masako Shima.

At first apparently pure olivine crystals were picked out from the beach sands or from the crushed rock samples. They were crushed into smaller grains, between 40 and 50 meshes in size. Under a binocular microscope, pure grains free from any inclusions were handpicked by means of a sharp pointed needle. About 100 to 200 mg sample was obtained from each specimen.

The Fo content of olivines was determined by the refractive indices, using the diagram by Poldervaart (1950) with the limit of the error of $\pm 1\%$.

Method of Analysis. About 10 mg of the sample was treated with 1 ml of 18 N sulfuric acid and 2 ml of 46% hydrofluoric acid, and the solution was heated to dryness in a platinum dish. After the addition of 2–3 ml of water, the solution was brought to dryness

again. The residue was dissolved in water and the solution was transferred into a beaker with small portions of 0.1 *N* hydrochloric acid. Evaporation was repeated with addition of 1 ml of nitric acid and then with 1 ml of hydrochloric acid, and the solution was transferred into a separatory funnel with 5 ml portions of 0.1 *N* hydrochloric acid and of 10% sodium acetate solution. Then the nickel was determined by the extraction and spectrophotometric method with dimethylglyoxime (Sandell, 1959). The fairly good agreement of the two determinations by using only a 10 mg-portion of a sample may indicate homogeneity of the samples.

Results and Discussion. The average of two determinations is given as the nickel content of an olivine, as given in Table I, together

Table I. Nickel and forsterite content of olivines

Sample No.	Occurrence	Forsterite mol. %	Nickel, wt. %			10 ³ Ni/Mg mol.
			Determined	Average		
604B	Nodule in basalt	86	0.229	0.240	0.235	3.46
100	"	90	0.330	0.331	0.321	4.48
2716	"	89	0.275	0.264	0.270	3.80
604C	"	88	0.246	0.253	0.250	3.62
701	"	87	0.235	0.245	0.240	3.51
H-A	Dunite	90	0.275	0.268	0.272	3.81
H-B	"	90	0.261	0.259	0.260	3.64
H-C	"	90	0.280	0.285	0.283	3.96
H-D	"	89	0.294	0.298	0.296	4.16
410	Phenocryst in tholeiite	89	0.376	0.356	0.366	5.16
305	"	89	0.255	0.301	0.278	3.98
243	"	84	0.091	0.087	0.089	1.37
37	"	84	0.146	0.140	0.143	2.20
36	"	82	0.133	0.142	0.138	2.17
2001	"	79	0.055	0.055	0.055	0.92
2809	"	78	0.029	0.027	0.028	0.47
Zaisho	Nodule in pallasite	81	0.023	0.020	0.021	0.34
Brenham	"	86	0.010	—	0.010	0.15

with the forsterite content (mol.%) optically determined. In Fig. 1, nickel content (wt.%) is plotted against the mol.% of Fo or 100 Mg/(Mg+Fe) atomic ratio. The nickel content of the olivines from pallasites is much lower than that of the olivines from terrestrial rocks. Except the pallasites, it is noticed that the nickel content of the olivines studied here lies on a relatively smooth curve, in spite of the difference in their origin. Nickel content of olivines in the volcanic rocks of pigeonitic rock series in Izu-Hakone district (Iida, Kuno and Yamasaki, 1961) and that of olivines in peridotite inclusions of alkalic basalts (Forbes and Banno, 1966) also lie on this curve. It is remarkable that the nickel content decreases so abruptly

Fig. 1. Variation in nickel contents of olivines of various origins against their composition.

- : Olivine nodule
- : Phenocryst in basalt
- ⊙: Dunite
- △: Pallasite
- : Skaergaard by Wager and Mitchell (1951)
- ▲: Hawaii Makaopuhi by Häkli and Wright (1967)
- : Peridotite inclusion of alkali basalts by Forbes and Banno (1966)
- ×: Pigeonitic rock series by Iida et al. (1961)
- ⊗: Hypersthene rock series by Iida et al. (1961)

that the content becomes almost zero at about 75 mol.% of forsterite. Olivines of Skaergaard intrusion (Wager and Mitchell, 1951) show a similar trend, though they shift toward more Fo-poor side by about 5–10 mol.%. Recently Häkli and Wright (1967) determined the nickel content in olivines from Makaopuhi lava lake of Hawaii, and its decreasing rate is much less than that shown in the present investigation. In contrast to these, the nickel content of olivines of volcanic rocks of the hypersthene rock series from Izu-Hakone district (Iida et al., 1961) is generally higher than those of the pigeonitic rock series and scatters in rather wide area.

In Fig. 2, the Ni/Mg atomic ratio is plotted against Fo mol.%

Fig. 2. Ni/Mg atomic ratios of olivines against their composition.

- : Nodule and dunite
 ●: Phenocryst in basalt
 ×: Pallasite

including the values of pallasites. It has already been pointed out by many investigators that the nickel content of olivines decreases with the decrease in magnesium content. In addition, the present investigation clearly demonstrates that the atomic ratio of Ni/Mg also decreases regularly with decrease in magnesium content of olivines.

Numerous explanations have been proposed for the sympathetic decrease of Ni with Mg in olivines. On the basis of the phase relations in the binary systems $\text{Mg}_2\text{SiO}_4\text{-Fe}_2\text{SiO}_4$ (Bowen and Schaier, 1935) and $\text{Ni}_2\text{SiO}_4\text{-Mg}_2\text{SiO}_4$ (Ringwood, 1956) a complete series of solid solutions is expected also in the ternary system $\text{Mg}_2\text{SiO}_4\text{-Ni}_2\text{SiO}_4\text{-Fe}_2\text{SiO}_4$, in which Ni_2SiO_4 lies between the other two components in its melting point. From these relations it is difficult, therefore, to explain why Ni content decreases abruptly with decrease of forsterite. Ringwood (1956) attributed the behavior of Ni to preferential replacement of Ni by Fe^{2+} in the olivine structure. Recently Burns and Fyfe (1966) have proposed a hypothesis of crystal-field stabilization energy of transition metals. Simple relations in binary system,

however, can not be extended to the crystallization in more complex basaltic liquids, in which transition metals are present both in octahedral and tetrahedral sites.

The genetic significance of this apparently abnormal behavior of Ni in olivines will be discussed elsewhere.

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References

- Bowen, N. L., and Schairer, J. F. (1935): The system MgO-FeO-SiO_2 . *Am. J. Sci.*, **29**, 151-217.
- Burns, R. G., and Fyfe, W. S. (1966): Behaviour of nickel during magmatic crystallization. *Nature*, **210**, 1147-1148.
- Forbes, R. B., and Banno, S. (1966): Nickel content of peridotite inclusion and cognate olivine from an alkali-olivine basalt. *Am. Min.*, **51**, 130-140.
- Häkli, T. A., and Wright, T. L. (1967): The fractionation of nickel between olivine and augite as a geothermometer. *Geochim. Cosmochim. Acta*, **31**, 877-884.
- Iida, C., Kuno, H., and Yamasaki, K. (1961): Trace elements in minerals and rocks of the Izu-Hakone region, Japan. Part I, Olivine. *J. Earth Sci., Nagoya Univ.*, **9**, 1-13.
- Poldervaart, A. (1950): Correlation of physical properties and chemical composition in the plagioclase, olivine, and orthopyroxene series, *Am. Min.*, **35**, 1067-1079.
- Ringwood, A. E. (1956): Melting relationships of Ni-Mg olivines and some geochemical implications. *Geochim. Cosmochim. Acta*, **10**, 297-303.
- Sandell, E. B. (1959): "Colorimetric Determination of Traces of Metals", 3rd. Ed., pp. 672.
- Wager, L. R., and Mitchell, R. L. (1951): The distribution of trace elements during strong fractionation of basic magma—a further study of the Skaergaard intrusion, East Greenland. *Geochim. Cosmochim. Acta*, **1**, 129-204.