GEIKIELITE FROM THE NÄÄTÄNIEMI SERPENTINITE MASSIF, KUHMO GREENSTONE BELT, FINLAND

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Abstract

Geikielite has only occasionally been reported as an accessory phase in metamorphosed, hydrothermally altered mafic and ultramafic rocks. This paper reports a new occurrence, in serpentinite of the Näätäniemi massif, in the Kuhmo greenstone belt, eastern Finland. Electron-microprobe analyses show that its composition ranges from $IIm_{20}Hem_2Gei_{60}Pyh_{18}$ to $IIm_{24}Gei_{56}Pyh_{20}$. The geikielite in these rocks is richer in Mn than that previously reported in serpentinized ultramafic rocks.

Keywords: geikielite, serpentinite, Näätäniemi, Kuhmo greenstone belt, Finland.

SOMMAIRE

Il est assez rare de rencontrer la geikielite comme phase accessoire dans les roches mafiques et ultramafiques qui ont subi des effets métamorphiques et métasomatiques. Nous en décrivons un exemple, d'une serpentinite du massif de Näätäniemi, dans la ceinture de roches vertes de Kuhmo, dans la partie orientale de la Finlande. Les analyses à la microsonde électronique montrent que sa composition varie de $IIm_{20}Hem_2Gei_{60}Pyh_{18}$ à $IIm_{24}Gei_{56}Pyh_{20}$. La geikielite dans ces roches est enrichie en Mn comparativement aux compositions documentées antérieurement dans les roches ultramafiques serpentinisées.

(Traduit par la Rédaction)

Mots-clés: geikielite, serpentinite, Näätäniemi, ceinture de roches vertes de Kuhmo, Finlande.

INTRODUCTION

The end members that comprise the ilmenite series in igneous and metamorphic rocks are ilmenite (FeTiO₃), hematite (Fe₂O₃), geikielite (MgTiO₃), pyrophanite (MnTiO₃), and ecandrewsite (ZnTiO₃) (Waychunas 1991). Significant solid-solution exists among the following end-members: 1) between ilmenite and hematite (IIm-Hem_{ss}), 2) between ilmenite and geikielite (IIm-Gei_{ss}), 3) between ilmenite and pyrophanite (IIm-Pyh_{ss}), and 4) between ilmenite and ecandrewsite (IIm-Eca_{ss}) (Haggerty 1976, Waychunas 1991).

Geikielite occurs predominantly in kimberlites, as xenocrysts derived by the crystallization of melts in the mantle (Haggerty & Thompkins 1984) and, less commonly, in carbonatites (Mitchell 1978), granulitegrade ferrous metapyroxenite lenses in gneisses (Scharbert 1979), in lenses of retrograded eclogite in gneisses (Pinet & Smith 1985, Smith & Pinet 1985), in serpentinized ultramafic rocks (Dietrich *et al.* 1986, Dymek *et al.* 1988, Windley *et al.* 1989), and in marble in contact aureoles (Gieré 1987). Geikielite has only occasionally been reported as an accessory phase in metamorphosed, hydrothermally altered mafic and ultramafic rocks. This brief report provides additional information on its chemistry and mode of occurrence in these rocks. In the course of our research on chromian spinel (Liipo *et al.* in prep.), minor amounts of geikielite were discovered in Archean metadunitic serpentinite from the Näätäniemi massif. This is the first reported occurrence of geikielite in Finland.

LOCATION AND GEOLOGICAL SETTING

The Kuhmo greenstone belt in eastern Finland (Taipale *et al.* 1980, Piirainen 1988) is a typical Archean greenstone belt surrounded by granitic rocks. It forms a composite north-trending belt approximately 20 km wide and 200 km long. The belt preserves upper-greenschist-facies assemblages and can be divided into three parts, namely the southern (Tipasjärvi), middle (between Kuhmo and Suomussalmi), and northern (Suomussalmi) areas (Fig. 1). It has been dated at between 2.99 (Vaasjoki &



FIG. 1. Geological sketch map of the Kuhmo greenstone belt. Modified after Taipale (1983) and Hanski (1984).

Sakko 1991) and 2.75 Ga (Vaasjoki *et al.* 1989) and is composed principally of volcanic rocks and, subordinately, of volcano-sedimentary and sedimentary rocks, which have been divided into three lithological units. Each unit is characterized by its own volcanic series: 1) andesite (Luoma group), 2) serpentinite – tholeiite – komatiite – basaltic komatiite (Kellojärvi group), and 3) rhyolite – rhyodacite – Fe-rich tholeiite – komatiite – basaltic komatiite (Ontojärvi group) (Taipale *et al.* 1980).

The ultramafic rocks have a multistage history, affected by at least three phases of deformation and two phases of intrusion of granitic magma, and are composed predominantly of serpentinite, having been deformed and metamorphosed under conditions of the greenschist or upper amphibolite facies (Piquet 1982, Taipale 1983, Blais & Auvray 1990, Tuisku & Sivonen 1984).

Petrography

In the samples collected from the Näätäniemi serpentinite massif, one sample of serpentinite was found to contain several small (6–15 μ m) grains of geikielite. This sample is dunitic in composition, and characterized by a metamorphic assemblage of lizardite and antigorite, and minor olivine (Fig. 2). Serpentine minerals were formed at the expense of olivine, which is extensively serpentinized, though minor amounts of olivine are still present. Accessory minerals include magnetite, Fe-rich chromite and geikielite. Magnetite occurs as anhedral grains, and chromite, as subhedral grains, within serpentine minerals. Geikielite is present as an inclusion in magnetite, and as composite grains with magnetite. Geikielite is grey under reflected light, and resembles ilmenite. On the basis of textures and occurrence, chromite is interpreted to be the only primary mineral in this sample.

ANALYTICAL PROCEDURES

The mineral analyses were performed with a wavelength-dispersion JEOL JCXA 733 electronmicroprobe equipped with LINK AN10 automation at the Institute of Electron Optics, University of Oulu. The acceleration voltage was 15 kV, the sample current, 15 nA, and the spot size, 2 μ m. A range of natural and synthetic standards were used (Alapieti & Sivonen 1983). Results were corrected with an on-line ZAF program. Ferrous and ferric iron were distributed on the basis of stoichiometry by the method of Carmichael (1967).

Owing to small grain-size of most of the geikielite grains, only analyses from grains 1 and 2 could be considered satisfactory, *i.e.*, not affected by adjacent minerals.

MINERAL CHEMISTRY

Geikielite occurs as small grains in or near the magnetite of the Archean serpentinite (Fig. 2). The two largest grains of geikielite found in this investigation are about 15 μ m in size, and homogeneous (Figs. 2, 3). Electron-microprobe analyses of geikielite (Fig. 4) reveal high contents of Mg and Mn, and lead to the compositions $IIm_{20}He_2Gei_{60}Pyh_{18}$ for grain 1 and $IIm_{22}He_2Gei_{54}Pyh_{22}$ for grain 2. (Table 1). On the basis of 6 atoms of oxygen, Mg, Mn²⁺ and Fe²⁺ amount to slightly more than 2 cations, and Ti is slightly less than 2 cations. Mg and Mn²⁺ seem to replace Fe²⁺ in the octahedral site. No Fe³⁺-bearing phases, such as magnetite and hematite, are present,



FIG. 2. Back-scattered electron image of geikielite (grain 1) and other small grains of geikielite, and their textural relationship with associated minerals. Symbols: GEI geikielite, MAG magnetite, OL olivine, and SRP serpentine. Scale bar: 50 μm.



FIG. 3. Back-scattered electron image of geikielite (grain 2) as an inclusion in magnetite. Symbols: GEI geikielite, MAG magnetite, SRP serpentine. Scale bar: 10 µm.

	1	2	3	4	5	6	
	Grain 1	Grain 2		small	grains		
	inclusion	inclusion		within	magnetite		
Wt%							
TiO ₂	57.56	56.60	59.14	58.97	58.13	57.67	
Fe ₂ O ₃	3.01	2.71	0.00	0.00	1.92	2.19	
FeO	11.13	12.07	13.09	12,44	11.33	10.39	
MnO	10.07	11.97	10.37	10.60	9.28	9.95	
MgO	18.60	16.54	16.67	16.80	18.29	18.25	
Total	100.36	99.89	99.2 7	98.81	98.94	98.45	
Number of ions based on 6 atoms of oxygen							
Ti	1.9087	1.9086	1.9894	1.9877	1.9431	1.9426	
Fe ³⁺	0.0998	0.0913	0.0000	0.0000	0.0641	0.0737	
Fe ²⁺	0.4102	0.4527	0.4897	0.4661	0.4210	0.3890	
Mn	0.3761	0.4545	0.3928	0.4025	0.3494	0.3777	
Mg	1.2225	1.1055	1.1112	1.1221	1.2115	1.2183	
Mg/R ²⁺	0.6086	0.5493	0.5574	0.5637	0.6113	0.6138	
	Mole	percent end	nember				
Ilmenite	19.92	21.98	24.56	23.41	20.90	10 24	
Hematite	2.42	2.22	0.00	0.00	1.58	1.82	
Geikielite	59.38	53,70	55.74	56.36	60.16	60.26	
Pyrophanite	18.26	22,08	19.69	20.21	17.34	18.68	

TABLE 1. REPRESENTATIVE COMPOSITIONS OF GEIKIELITE GRAINS, NÄÄTÄNIEMI SERPENTINITE MASSIF

 $Mg/R^{2+} = Mg/(Mg+Mn+Fe^{2+})$

either as inclusions or as exsolution lenses in geikielite. Calculations of stoichiometry indicate small amounts of Fe^{3+} in the geikielite.

Olivine ranges in composition from Fo_{95} to Fo_{96} , and is extensively altered to lizardite. The relatively high value for MgO and MnO (Table 2) indicates that the olivine is metamorphic in origin (*e.g.*, Piquet 1982, Blais & Auvray 1990).

The chromite grains are compositionally zoned from core to rim. The decrease in level of Cr from

TABLE 2. REPRESENTATIVE COMPOSITION OF MAGNETITE, CHROMITE AND OLIVINE OCCURRING IN THE SAME SAMPLE AS THE GEIKIELITE

	1	2	3	4	5		
	Magnetite	Magnetite _		Chromite	_	Olivine	
	with gei 1	with gei 2	core	rim I	rim II		
Wt%							
SiO ₂	+	-	-	-	-	42.28	
TiO ₂	1.13	0.22	1.63	0.78	0.22	-	
Cr ₂ O ₃	1.77	2.11	37.05	11.44	3.23	-	
Fe2O3	66.35	67.96	29.75	57.18	65.15	-	
FeO	29.41	28.69	19.95	25.90	29.31	3.48	
MnO	0.50	0.36	6.13	2.46	0.43	0.98	
MgO	1.59	1.69	3.66	2.27	1.49	54.78	
ZnO	0.15	0.00	2.34	0.56	0.00	-	
Total	100.90	101.04	100.61	100.62	99.83	101.52	
Number of ions based on 32 (chromite and magnetite) and 4 atoms of oxygen (olivine)							
Si	-	-	-	-	-	0.9934	
Ti	0.2534	0.0493	0.3566	0.1737	0.0517		
Cr	0.4187	0.4979	8.5333	2.6912	0.7798	-	
Fe ³⁺	14.914	15.248	6.5200	12.808	14.975		
Fe ²⁺	7.3478	7.1529	4.8596	6.4464	7,2300	0.0685	
Mn	0.1259	0.0904	1.5125	0.6212	0.1109	0.0196	
Mg	0.7092	0.7515	1.5886	1.0075	0.6774	1 9185	
Zn	0.0322	0.0000	0.5033	0.1228	0.0000		
x _{Mg}	0.0880	0.0391	0.2464	0.1352	0.0857	0.9655	

Properties of Fe²⁺ and Fe³⁺ are allotted according to stoichiometry in the case of spinel-group phases. $X_{Mg} = Mg/(Mg+Fe^{2+})$

core to rim is correlated with decrease in concentration of Mg, Mn, and Ti. An interesting feature of the chemistry of the chromite in the same samples as the geikielite is the high Mn content found in their core (up to 6.13 wt% MnO).

The magnetite enclosing the geikielite shows no difference compared to other grains of magnetite occurring in the same sample; it contains a relatively high level of Mg (Table 2).

The main serpentinite minerals are lizardite and antigorite, the former corresponding to the lizardite II described by Blais & Auvray (1990).

DISCUSSION

Geikielite should be expected only in extremely magnesian assemblages, in which Mg/(Mg + Fe²⁺) $[X_{Mg}]$ in spinel is at least 0.90 (Windley *et al.* 1989) or olivine is more magnesian than Fo₉₅ (Frost 1991). In the sample studied, the X_{Mg} value of the chromite ranges from 0.26 in the core to 0.08 in the outer rim, and olivine compositions range from Fo₉₅ to Fo₉₆.

Because of extensive metamorphism, which has obliterated all primary textures, it is unclear if geikielite represents the product of recrystallization of an ilmenite poorer in Mg or a primary igneous ilmenite solid-solution. Its occurrence as an inclusion in magnetite and as composite grains with magnetite, and its chemical composition, suggest that in these rocks, the geikielite is a result of metamorphic and hydrothermal processes, as the Mn and Mg contents of primary ilmenite from mafic rocks are usually low, 0.1 - 2.3 wt% MgO, and 0.1 - 1.4 wt% MnO (Frost & Lindsley 1991).

TABLE 3. REPRESENTATIVE COMPOSITIONS OF GEIKIELITE REPORTED FROM METAMORPHOSED ULTRAMAFIC ROCKS

	1	2	3	4			
Wt%							
TiO ₂	58.26	57.65	62.13	60.13			
FeO	29.48	28.92	15.14	16.01			
MnO	0.83	2.32	1.05	5.00			
MgO	11.48	11.42	21,89	18.94			
Total	100.05	100.31	100.21	100.08			
Number of ions based on 6 atoms of oxygen							
Ti	2.0204	2.0023	2.0073	1.9902			
Fe ²⁺	1,1369	1.1170	0.5439	0.5893			
Mn	0.0324	0.0908	0.0382	0.1864			
Mg	0.7890	0.7861	1.4017	1.2424			
Mg/R ²⁺	0.4029	0.3943	0.7066	0.6156			
Mole percent end member							
Ilmenite	58.05	56.02	27.42	29.19			
Hematite	0.00	0.00	0.00	0.00			
Geikielite	40.29	39.42	70.65	61.56			
Pyrophanite	1.65	4.55	1.92	9.23			

1 - 3 : Windley et. al. (1989), 4 : Dietrich et al. (1986).



FIG. 4. Chemical compositions of geikielite in the Näätämiemi serpentinite massif. The compositions of Dietrich *et al.* (1986) and Windley *et al.* (1989) are plotted for comparison.

Compared with other examples of geikielite (Fig. 4, Table 3) reported from metamorphosed ultramafic rocks (Dietrich *et al.* 1986, Windley *et al.* 1989), the geikielite reported in this paper has a higher Mn content, which seems to increase with Mg at the expense of Fe in the octahedral site. The relatively high component of pyrophanite in geikielite indicates that there is extensive solid-solution between these phases.

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REFERENCES

- ALAPIETI, T. & SIVONEN, S. (1983): Use of the electron microprobe in the investigation of the Early Proterozoic Koillismaa layered igneous complex, NE Finland. Geol. Surv. Finland, Rep. Invest. 61.
- BLAIS, S. & AUVRAY, B. (1990): Serpentinization in the Archean komatiitic rocks of the Kuhmo greenstone belt, eastern Finland. *Can. Mineral.* 28, 55-66.
- CARMICHAEL, I.S.E. (1967): The iron-titanium oxides of salic volcanic rocks and their associated ferromagnesian silicates. *Contrib. Mineral. Petrol.* 14, 36-64.

- DIETRICH, H., KOLLER, F., RICHTER, W. & KIESL, W. (1986): Petrologie und Geochemie des Rodingitvorkommens vom Islitzfall (Dorfertal, Hohe Tauern). Schweiz. Mineral. Petrogr. Mitt. 66, 163-192.
- DYMEK, R.F., BROTHERS, S.C. & SCHIFFRIES, C.M. (1988): Petrogenesis of ultramafic metamorphic rocks from the 3800 Ma Isua supracrustal belt, West Greenland. J. Petrol. 29, 1353-1397.
- FROST, R.B. (1991): Stability of oxide minerals in metamorphic rocks. *In* Oxide Minerals: Petrologic and Magnetic Significance (D.H. Lindsley, ed.). *Rev. Mineral.* 25, 469-487.
- & LINDSLEY, D.H. (1991): Occurrence of irontitanium oxides in igneous rocks. *In* Oxide Minerals: Petrologic and Magnetic Significance (D.H. Lindsley, ed.). *Rev. Mineral.* 25, 433-468.
- GIERÉ, R. (1987): Titanian clinohumite and geikielite in marbles from the Bergell contact aureole. Contrib. Mineral. Petrol. 96, 496-502.
- HAGGERTY, S.E. (1976): Opaque mineral oxides in terrestial igneous rocks. In Oxide Minerals (D. Rumble III, ed.). Rev. Mineral. 3, Hg101-300.
- & THOMPKINS, L.A. (1984): Subsolidus reactions in kimberlitic ilmenites: exsolution, reduction and the redox state of the mantle. *In* Kimberlites. I. Kimberlites and Related Rocks (J. Kornprobst, ed.). Elsevier, Amsterdam, The Netherlands (335-357).
- HANSKI, E. (1984): The Gabbro-Wehrlite Association in the Eastern Part of the Baltic Shield. Phil. Lic. thesis, Univ. of Oulu, Oulu, Finland.

- MITCHELL, R.H. (1978): Manganoan magnesian ilmenite and titanian clinohumite from the Jacupiranca carbonatite, São Paulo, Brazil. Am. Mineral. 63, 544-547.
- PIIRAINEN, T. (1988): The geology of the Archaean greenstone-granitoid terrain in Kuhmo, eastern Finland. Geol. Surv. Finland, Spec. Pap. 4, 39-51.
- PINET, M. & SMITH, D.C. (1985): Petrochemistry of opaque minerals in eclogites from the Western Gneiss region, Norway. 1. Petrology of the oxide micro-assemblages. *Chem. Geol.* 50, 225-249.
- PIQUET, D. (1982): Mécanismes de recristallisations métamorphiques dans les ultrabasites: exemple des roches vertes archéennes de Finlande orientale (Ceinture de Suomusalmi - Kuhmo). Thèse de 3ème cycle, Université de Rennes, Rennes, France.
- SCHARBERT, H.G. (1979): Mg-reicher Ilmenit in einem Granatwebsterit im Granulitkörper von St. Leonard, Mittleres Kamptal, Niederösterreich. Anzeig. öster. Akad. der Wissen. 116, 161-165.
- SMITH, D.C. & PINET, M. (1985): Petrochemistry of opaque minerals in eclogites from the Western Gneiss region, Norway. 2. Chemistry of the ilmenite mineral group. *Chem. Geol.* 50, 251-266.
- TAIPALE, K. (1983): The geology and geochemistry of the Archaean Kuhmo greenstone-granite terrain in the Tipasjärvi area, eastern Finland. Acta Univ. Oulu A 151, Geol. 5.

- _____, TUOKKO, I. & PIIRAINEN, T. (1980): A brief introduction in the geology and geochemistry of the Kuhmo greenstone belt, eastern Finlancl. In Nickel Sulfides in Ultramafic and Mafic Rocks (H. Papunen, ed.). IGCP Project 161, Field Excursion Guidebook, 37-73.
- TUISKU, P. & SIVONEN, S. (1984): Paine- ja lämpötilaolosuhteet Kuhmon vihreäkivivyöhykkeen metamorfoosissa (Geothermometry, geobarometry and metamorphic conditions in the Kuhmo greenstone belt). Univ. of Oulu, Oulu, Finland (19 p.).
- VAASJOKI, M. & SAKKO, M. (1991): Isotopic constraints on the age and genesis of the Finnish greenstone belts and their ore deposits. *In* The Types, Evolutionary Epochs and Metallogeny of Greenstone Belts; Soviet – Finnish Symp. (Kostomuksha), Abstr., 15-16.
- , WARD, P. & LAVIKAINEN, S. (1989): U-Pb zircon ages from the late Archaean Hattu schist belt, eastern Finland. *Geol. Surv. Finland, Spec. Pap.* **10**, 33-36.
- WAYCHUNAS, G.A. (1991): Crystal chemistry of oxides and oxyhydroxides. In Oxide Minerals: Petrologic and Magnetic Significance (D.H. Lindsley, ed.). Rev. Mineral. 25, 11-68.
- WINDLEY, B.F., HERD, R.K. & ACKERMAND, D. (1989): Geikielite and ilmenite in Archean meta-ultramafic rocks, Fiskenaesset, West Greenland. *Eur. J. Mineral.* 1, 427-437.
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