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^{13}C-depleted moissanites in subduction-related rocks: tracers of slab fluids in the Earth's mantle and a new diamond exploration tool

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Abstract. A magnesian low-Ti shoshonite dike intruding Archean Norwegian Terrane includes numerous grains of black, blue and gray moissanite (SiC). Moissanite contains inclusions of native Si, Fe and Al, Fe-Cr carbides, Fe-Cr-Mn alloys and diamond. The range of observed $\delta^{13}C$ values (-24.8 to -29.6‰) is similar to ophiolite-hosted SiC, lower mantle diamonds and slab-derived biogenic carbon. Norwegian moissanites may have been formed during interaction of Earth's mantle with carbonaceous slab fluids under extremely reducing conditions as suggested by native metal and carbide inclusions. ^{13}C-depleted moissanite can be used as a new exploration tool for sub-lithospheric diamonds in Archean to Phanerozoic accreted terranes and mobile belts.

Moissanite (SiC) occurs in kimberlites, alkaline basalts, podiform chromitites in ophiolites and inclusions in diamonds [1-3]. Thermodynamic data suggest formation at high pressures and temperatures in an extremely reducing environment, 5-8 log units below the iron-wüstite buffer, which is the lowest level of fO_2 activity in the lithospheric mantle [4]. This, together with common association with diamond, abundance of native metal and metal carbide inclusions and ^{13}C-depleted isotope composition, led several authors to propose lower mantle or transitional zone origin for natural moissanite [3,5]. Lower pressure origin has been also hypothesized on the basis of thermodynamic modeling and rare occurrence in crustal rocks [6]. Ubiqutous presence of moissanite and diamond in podiform chromites from Tethyan and Uralian ophiolites in association with crustal minerals (Table 1) is interpreted as evidence for superdeep mantle-crust interactions in sudbuction zones and recycling of slab components into various mantle reservoirs [2,3].

We report in this paper new data on moissanite from a primitive Mg-rich shoshonite from eastern Finnamark, Norway. Shoshonitic dike (14-18 wt.% MgO, K/Na >1, TiO_2 < 0.60 wt.%) intrudes Archean (2.5-3.69 Ga) felsic gneisses of the Norwegian Cratonic Terrane near the villages of Neiden and Bugoyfjord in the Sör-Varanger area of eastern Finnamark [7]. Shoshonite dike is an intensely porphyritic volcanic rock composed of mica, primary pargasitic amphibole and chrome diopside phenocrysts and megacrysts (Table 2).

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Accessory phases include zircon, apatite, ilmenite, magnetite, Cr-magnetite, titanite, rutile and spinal (table 2).

Table 1. Occurrence of moissanite in subduction-related rocks.

	Norway (this work)	**Ophiolites in Tibet, Urals and Tethyan belt [2,3]**
Host rocks	Mg-shoshonite	Chromitite
Associated minerals	Phlogopite, high-Cr pargasitic amphibole, Mn-rich ilmenite, Sr-bearing Al-Fe-Mg spinel, Cr-magnetite, corundum, Ba-rutile, high-Al titanite	Rutile, zircon, corundum, native Si-Al-Cr-Ni-W, Si-W-carbides, Cr-Fe-Si-Al-Ni-Co-Mn-Sn-Cu alloys, high Al-titanite, coesite, kyanite, wüstite, escolaite, ilmenite, baddeleyite
Inclusions	Diamond, native Si and Al, Fe-Cr carbides	No inclusions reported in moissanite; associated diamonds contain coesite, Ni-Mn-Co alloys, Mn-garnet, Mn-olivine, MnO
$\delta^{13}C$ (‰)	- 24.8 to -29.6	-18.3 to -28.7

Mn-rich ilmenites and high-Al titanites are compositionally similar to inclusions in some lower mantle diamonds, while Ba-rutile and Sr-bearing Al-Fe-Mg spinel were interpreted as metasomatic phases comparable to kimberlitic and lamporitic lithospheric sources [8]. Geochemical signatures such as LILE-enrichment coupled with clear HFSE (Ta, Nb, Ti, Zr) depletion suggest derivation from a mantle wedge source metasomatized by slab-derived fluids [7].

Table 2. Selected microprobe analyses (wt.%) of minerals in shoshonite from Norway.

	Mn-Ilm	**Cr-Mt**	**Titanite**	**Spinel**	**Rutile**	**Cpx**	**Amph**	**Mica**
SiO_2	0.02	0.82	31.8	0.09	0.08	51.2	44.8	36.1
TiO_2	51.2	1.59	30.9	0.26	96.1	0.38	1.54	4.12
Al_2O_3	0.01	0.11	5.78	11.8	0.03	5.13	9.70	14.9
Cr_2O_3	0.00	1.01	0.00	47.4	0.00	2.07	1.01	0.00
FeO	31.7	93.5	1.13	36.1	2.23	5.45	14.3	15.5
MnO	15.3	0.01	0.02	0.23	0.11	0.22	0.17	0.09
MgO	0.02	0.04	0.35	1.38	0.00	16.7	12.2	13.6
CaO	0.20	0.24	28.4	0.03	0.72	18.3	11.7	0.55
Na_2O	0.02	0.10	0.00	0.00	0.06	0.58	1.55	0.22
K_2O	0.06	0.04	0.08	0.02	0.05	0.14	0.64	8.56
Nb_2O_5	0.02	0.00	0.00	0.00	0.05	0.00	0.00	0.40
BaO	0.56	0.00	0.28	0.00	0.95	0.00	0.20	0.17
SrO	0.01	0.08	0.10	2.23	0.01	0.14	0.00	0.05
Total	99.1	100.4	98.7	99.5	100.4	100.3	97.7	94.2

Note. Mn-Ilm- Mn-rich ilmenite, Cr-Mt- chrome magnetite, Cpx- clinopyroxene, Amph- amphibole. Analyses acquired using Cameca SX5 EPMA at the Center for Nano-Studies, University of Florida, Gainesville, Florida, USA. Operating conditions: accelerating voltage of 14 keV, sample current of 20 nA and counting times of 10 to 30 seconds.

More than 30 crystals (0.1 to 1mm) of hexagonal moissanite were recovered from a 51.2 kg sample of magnesian Bugofjord shoshonite using a standard caustic fusion method at the MSA Group Laboratories in Johannesburg, South Africa. Moissanites are black, grey, or light and dark blue, with distinct peaks on the Raman spectra (Figure 1). Several dark and light blue grains contain inclusions of diamond, native Si, Al and Fe, Fe-Cr-Mn alloys, Fe-Cr carbides and possibly periclase (Figure 2). This assemblage is similar to metal-rich inclusions reported from lower mantle diamonds in kimberlites [8]. Several grains of black and blue moissanite were analyzed for carbon isotopes (Table 3)

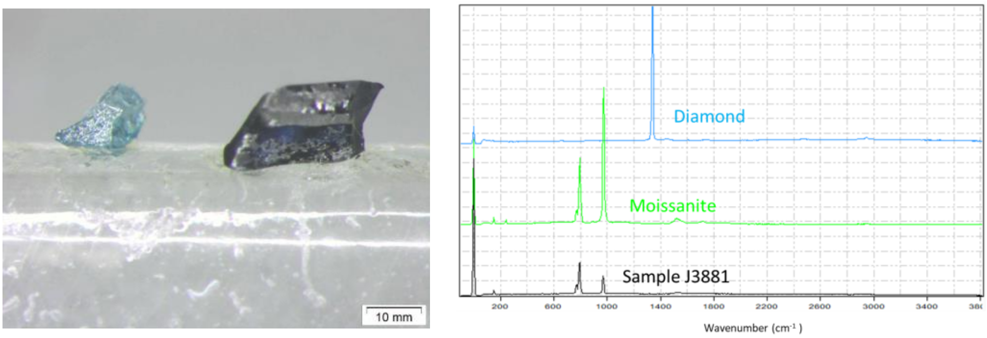

Fig. 1. Blue and black hexagonal moissanite (SiC) from shoshonite sample J3881. Raman data obtained using a WITec alpha300R Confocal Laser Raman Microscope at the University of Johannesburg, RSA.

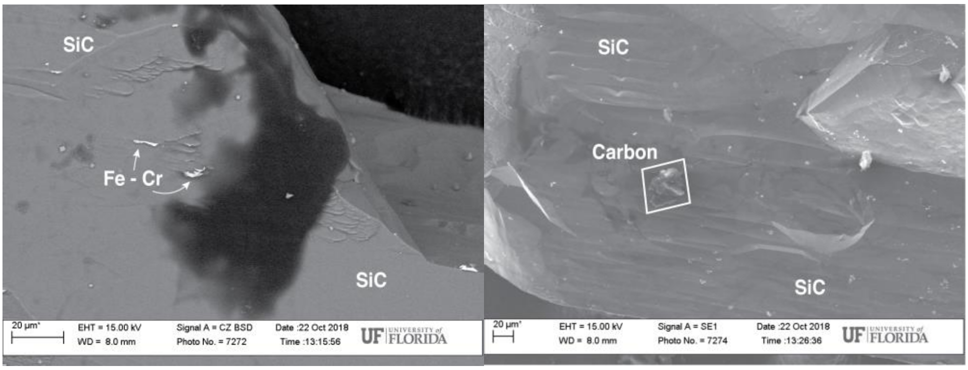

Fig. 2. Backscatter SEM images of inclusions in moissanite (left image – Fe-Cr carbides, right image – diamond).

Table 3. Carbon isotope composition of moissanite (SiC) from the Norwegian shoshonite.

Grain#	Color	δ^{13}C (‰)
2/4-1	Black	-25.5
2/4-2	Black	-27.8
1/4-5	Black	-29.6
1/4-6	Black	-24.8
1/4-9	Large black	-25.6
2/4-3	Blue	-27.1
2/4-4	Blue	-27.1
1/4-7	Blue	-27.4
1/4-8	Blue	-28.0

Analyses performed at the iThemba Laboratories, Johannesburg, South Africa.

All analyzed crystals are strongly depleted in ^{13}C independently of their color, crystal appearance or inclusion assemblage (Table 3, Figure 3). The range of observed $\delta^{13}C$ values (-24.8 to -29.6‰) in Norwegian moissanites is similar to that reported for several suites of kimberlitic diamonds and carbides (with proven lower mantle origin) as well as to the ^{13}C-depleted signature of biogenic carbon [2,3,9].

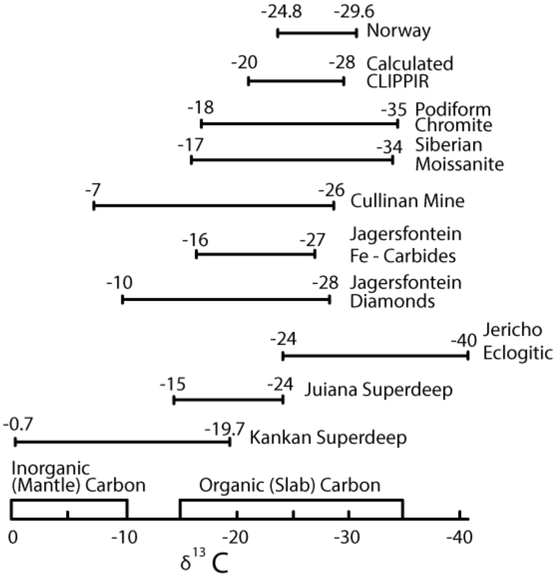

Fig. 3. Carbon isotope compositions of Norwegian moissanites compared to lower mantle diamonds from Kankan, Guinea [10] and Juina, Brazil [8], eclogitic diamonds from the Jericho mine [11], sub-lithospheric diamonds from Jagersfontein and Cullinan [12] mines, diamonds from ophiolitic podiform chromitites [2] and moissanites from Siberian kimberlites [5]. Calculated values for CLIPPIR reservoir are from [13], for inorganic (mantle) and organic (slab) carbon - from [9,14].

This ^{13}C depletion observed in both lithospheric and sub-lithospheric carbon-based mineral species has been interpreted as evidence for recycling of biogenic carbon derived from subducted slab into the Earth's mantle [2,9,14]. Occurrence of Si-Al-Mn-K inclusions coupled with ^{13}C-depleted (biogenic) isotopic signature in the Norwegian moissanite most likely reflects formation in the presence of slab-derived fluids in an extremely reduced environment in the Earth's mantle. Under this scenario, metal-saturated (Fe, Cr, Mn, Al) lower mantle assemblages will act as a reducing medium during interaction with carbonaceous fluids derived from deeply subducted lithospheric slabs [2,3,8]. Enrichment of these deep fluids in Si, C, Ca, Mn and Al may lead to the formation of lower mantle moissanite and diamond along with the observed suite of native metal, alloys and carbide inclusions [2,3].

Severe ^{13}C depletion in the lower mantle has been linked to the so-called CLIPPIR (Cullinan-like, Large, Inclusion-Poor, Pure, Irregular, and Resorbed) diamond reservoir believed to be the source for large diamonds of exceptional quality and value (such as Cullinan, Constellation, Koh-i-Noor) as well as very rare blue ("boron-spiked") diamonds [15]. Isotopically light SiC from the Norwegian shoshonite may have been formed under conditions similar to that observed in the CLIPPIR diamond reservoir.

We propose that moissanites characterized by a combination of metal (Si-Al-Fe) and carbide (Fe-Cr-Mn) inclusions and a ^{13}C depletion signature ($\delta^{13}C$ > 20‰) can be successfully used as a new diamond exploration tool to locate primary sources of sub-lithospheric diamonds, possibly of exceptional value (originated from a CLIPPIR lower mantle reservoir), size and/or color. Moissanites of this type can be used to search for diamond deposits in Archean craton and off-craton settings as well as Phanerozoic mobile belts and accreted terranes.

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