Minohlite, a new copper-zinc sulfate mineral from Minoh, Osaka, Japan

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ABSTRACT

Minohlite, a new copper-zinc sulfate mineral related to schulenbergite, was found in the oxidized zone of the Hirao mine at Minoh (Minoo) City, Osaka Prefecture, Japan. The mineral occurs in cracks in altered shale as rosette aggregates up to 100 μm in diameter, composed of hexagonal platy crystals up to 50 μm in diameter and 10 μm in thickness. The associated minerals are chamosite, muscovite, smithsonite, serpierite, ramsbeckite, 'limonite' and chalcopyrite. Minohlite has hexagonal (or trigonal) symmetry with unit-cell parameters of $a = 8.2535(11)$, $c = 8.1352(17)$ Å, $V = 479.93(16)$ Å^3 and $Z = 1$, and possible space groups $P6$, $P\bar{6}$, $P6/m$, $P622$, $P6mm$, $P\bar{6}2m$ and $P6/mmm$ (or $P3$, $P\bar{3}$, $P321$, $P3m1$, $P\bar{3}m1$, $P312$, $P31m$ and $P\bar{3}1m$). The six strongest reflections in the powder X-ray diffraction pattern [d in Å (I) hkl] are 8.138 (20) 001; 4.128 (24) 110; 2.702 (100) 120; 2.564 (76) 121; 1.560 (43) 140; and 1.532 (24) 141. Electron microprobe analyses gave the following values (wt.%): CuO 37.18, ZnO 21.08, FeO 0.49, SO$_3$ 16.78, SiO$_2$ 0.44, and H$_2$O 24.03 (by difference). The empirical formula, calculated on the basis of Cu + Zn + Fe + S + Si = 9 atoms per formula unit, is (Cu$_{4.43}$Zn$_{2.45}$Fe$_{0.06}$)$_{\Sigma6.94}$[(SO$_4$)$_{1.99}$(SiO$_4$)$_{0.07}$]$_{\Sigma2.06}$(OH)$_{9.64}$·7.81H$_2$O, which leads a simplified formula of (Cu,Zn)$_7$(SO$_4$)$_2$(OH)$_{10}$·8H$_2$O where Cu > Zn. The mineral is bluish-green and transparent with a pearly to vitreous lustre. The streak is pale green. Cleavage is perfect on {001}. The Mohs hardness number is less than 2. The calculated density is 3.28 g cm^{-3}. The mineral is named after Minoh City, where it was discovered.

Keywords: minohlite, new mineral, schulenbergite, sulfate, Hirao mine, Minoh.

Introduction

In June 1999, during a mineralogical survey on secondary minerals at the Hirao mine, Japan, one of the authors (M.O.) collected a bluish-green mineral. Preliminary powder X-ray diffraction studies indicated that the mineral was different from any known minerals or synthetic materials. The mineral was referred to as an "unidentified mineral associated with ramsbeckite" by Ohnishi *et al.* (2004). Subsequent studies revealed that the mineral is a new species of copper-zinc sulfate.
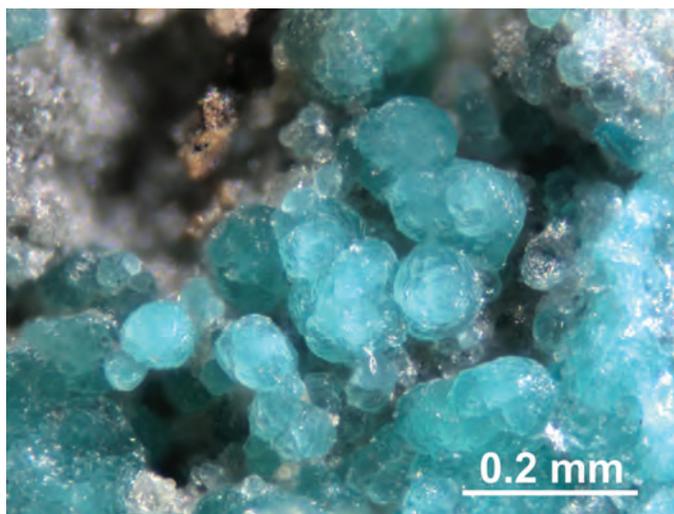
FIG. 1. Photomicrograph of rosette aggregates of minohlite from the Hirao mine (#NSM-M43670).

The new mineral was named minohlite after Minoh City, where the Hirao mine is located; although the city is sometimes referred to as 'Minoo' (e.g. Matsuura *et al.*, 1995; Ohnishi *et al.*, 2002), the official name used by the city government is 'Minoh'. The mineral data and name were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2012-035). Type specimens of minohlite are deposited in the collections of the National Museum of Nature and Science, Tsukuba, Japan [#NSM-M43670 (holotype) and #NSM-M43671

(cotype)] and the Kyoto University Museum, Kyoto, Japan [#KUM-M00001 (cotype)].

Occurrence

The Hirao mine (34º50′N, 135º28′E) is located at Onsen-cho (formerly Hirao), Minoh City, Osaka Prefecture, Japan. The ore deposit of the mine is developed in shale that includes lenses of sandstone and chert belonging to the Jurassic Tamba terrane (Matsuura *et al.*, 1995). The host rock consists of chamosite which formed during hydrothermal alteration. The predominant ore
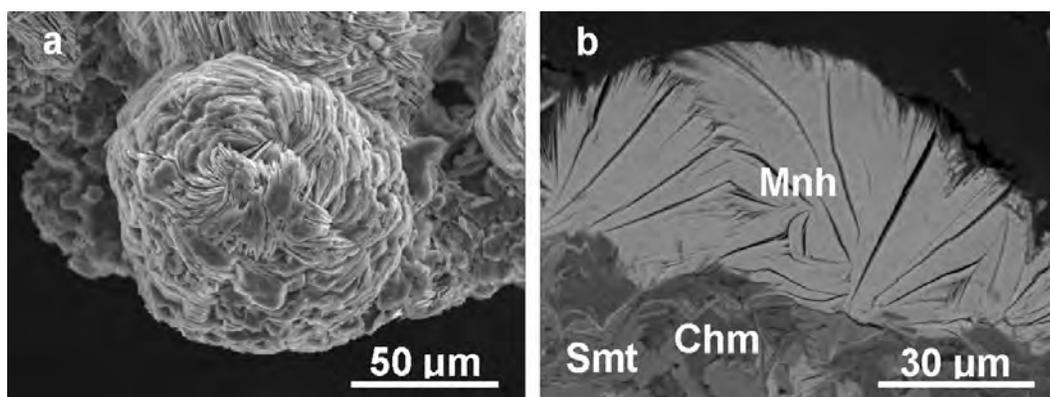
FIG. 2. SEM image (*a*) and BSE image (*b*) of minohlite from the Hirao mine. Abbreviations: Mnh = minohlite, Smt = smithsonite, Chm = chamosite

mineral is sphalerite with lesser amounts of chalcopyrite, pyrite and galena distributed throughout the altered shale. In the oxidized zone of the deposit, rare Cu- and/or Zn-dominant secondary minerals such as brianyoungite (Ohnishi *et al.*, 2001), ktenasite (Ohnishi *et al.*, 2002), ramsbeckite (Ohnishi *et al.*, 2004), schulenbergite and its Zn-dominant analogue (Ohnishi *et al.*, 2007a) and osakaite (Ohnishi *et al.*, 2007b) have been found.

Minohlite was found in cracks in altered shale at the oxidized zone. The mineral occurs very rarely as rosette aggregates up to 100 μm in diameter, composed of hexagonal platy crystals up to 50 μm in diameter and 10 μm in thickness but usually 30 μm in diameter and 1 μm in thickness (Figs 1, 2 and 3a). The associated minerals are chamosite, muscovite, smithsonite, serpierite, ramsbeckite, 'limonite' and chalcopyrite. Minohlite is similar in appearance and occurrence to schulenbergite. Minohlite might have formed as a secondary mineral deposited from underground water containing Cu^{2+}, Zn^{2+} and SO_4^{2-} ions derived from the dissolution of chalcopyrite and sphalerite.
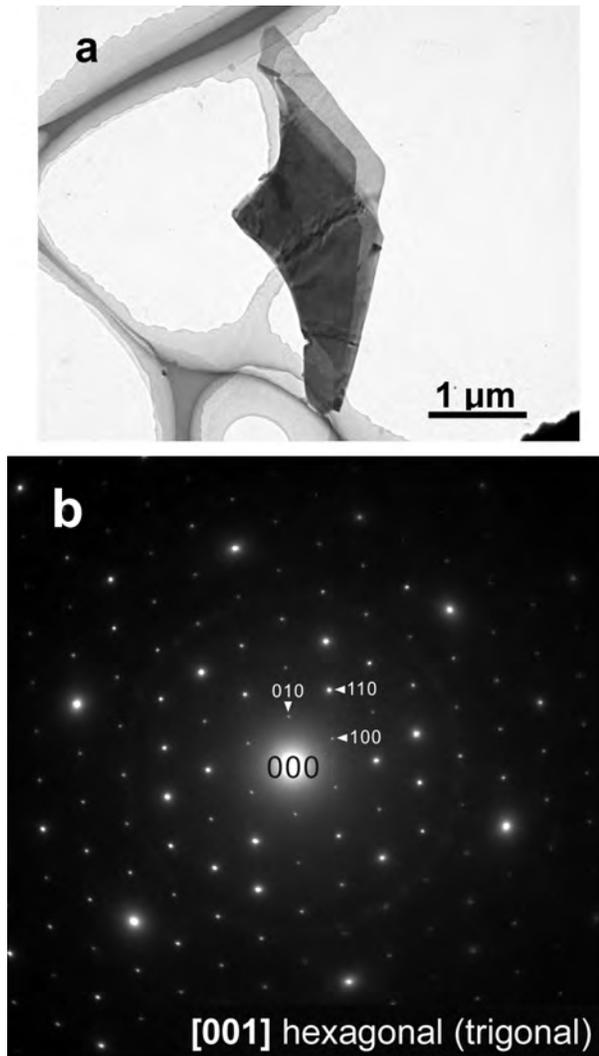
FIG. 3. Bright-field TEM image of the fragment of minohlite crystals (*a*) and its SAED pattern (*b*).

Physical and optical properties

Minohlite is bluish-green and is transparent with a pearly to vitreous lustre. The streak is pale green. Cleavage is perfect on {001}. Tenacity is brittle. The mineral is very soft, with a Mohs hardness number of <2. The density was measured by flotation of the rosette aggregates in Clerici solution. The measured density is 3.39(2) g cm^{-3}, although a small amount of smithsonite ($D_{calc.} \approx 4.37$ g cm^{-3}) could not be perfectly separated from the minohlite. The calculated density, using the empirical formula and the refined unit-cell parameters, is 3.28 g cm^{-3}. No fluorescence is observed under short- or long-wavelength ultraviolet light. Minohlite is optically anisotropic, and moderate birefringence is observed in thin section. No pleochroism is exhibited. Further optical properties could not be determined because of the small crystal size and the small quantity of the sample available. The mineral is easily soluble in dilute hydrochloric acid.

Crystallography

Single-crystal X-ray diffraction studies of minohlite could not be carried out because of the small crystal size. Powder X-ray diffraction data of the mineral were measured using a synchrotron X-ray source (λ = 0.41114 Å) with Debye-Scherrer geometry at the AR-NE1 beam line, Photon Factory, High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. The diffraction data were recorded using an imaging plate detector. Observed intensities in the two-dimensional diffraction image were integrated along a circumference direction with respect to the same 2θ and converted to conventional one-dimensional diffraction profiles using the programs IPAnalyzer and PDIndexer (Seto *et al.*, 2010). Although a small amount of smithsonite is present in the measured material, the diffraction pattern can be indexed on a hexagonal (or trigonal) cell with *a* = 8.2535(11), *c* = 8.1352(17) Å, *V* = 479.93(16) Å^3, and *Z* = 1. The data of indexed reflections are listed in Table 1. The unit cell was confirmed by a selected area electron diffraction (SAED) pattern obtained with a JEOL JEM-2010F transmission electron microscope (TEM) using an accelerating voltage of 200 kV at ISSP of the University of Tokyo. The bright-field TEM image and SAED pattern of minohlite are shown in Fig. 3. The SAED pattern

indicated hexagonal (or trigonal) symmetry. It can be indexed to the hexagonal [001] zone (Fig. 3*b*). These findings suggest that the possible space groups of minohlite are *P*6, *P*6̄, *P*6/*m*, *P*622, *P*6*mm*, *P*6̄2*m* and *P*6/*mmm* (or *P*3, *P*3̄, *P*321, *P*3*m*1, *P*3̄*m*1, *P*312, *P*31*m* and *P*3̄1*m*).

Infrared spectrometry

A Fourier transform-infrared absorption (FTIR) spectrum of minohlite was recorded with a KBr pellet method on a JASCO MFT-680 FTIR spectrometer for the region from 4000 cm^{-1} to 400 cm^{-1} (Fig. 4). The strong absorption bands at around 3422 cm^{-1} are attributed to the O−H stretching vibration, and the weak absorption at

TABLE 1. Representative powder X-ray diffraction data for minohlite from the Hirao mine.

h	k	l	$d_{calc.}$	$d_{meas.}$	I
0	0	1	8.135	8.138	20
1	0	0	7.148	7.151	7
1	0	1	5.370	5.373	8
1	1	0	4.127	4.128	24
1	1	1	3.680	3.680	10
2	0	1	3.272	3.276	6
1	1	2	2.897	2.900	6
1	2	0	2.702	2.702	100
1	2	1	2.564	2.564	76
3	0	0	2.383	2.382	9
1	2	2	2.250	2.252	8
2	2	0	2.063	2.064	5
3	0	2	2.056	2.057	5
0	0	4	2.034	2.034	4
1	3	0	1.982	1.983	6
2	2	2	1.840	1.840	5
4	0	1	1.745	1.744	8
2	3	0	1.640	1.639	6
0	0	5	1.627	1.627	5
1	2	4	1.625	1.627	4
2	3	1	1.608	1.608	4
1	0	5	1.587	1.586	5
1	4	0	1.560	1.560	43
1	4	1	1.532	1.532	24
1	1	5	1.514	1.512	10
1	4	2	1.456	1.457	4
1	2	5	1.394	1.393	4
2	4	0	1.351	1.351	12
2	4	1	1.333	1.333	11
1	0	6	1.332		
3	3	2	1.303	1.303	4
2	4	2	1.282	1.281	6
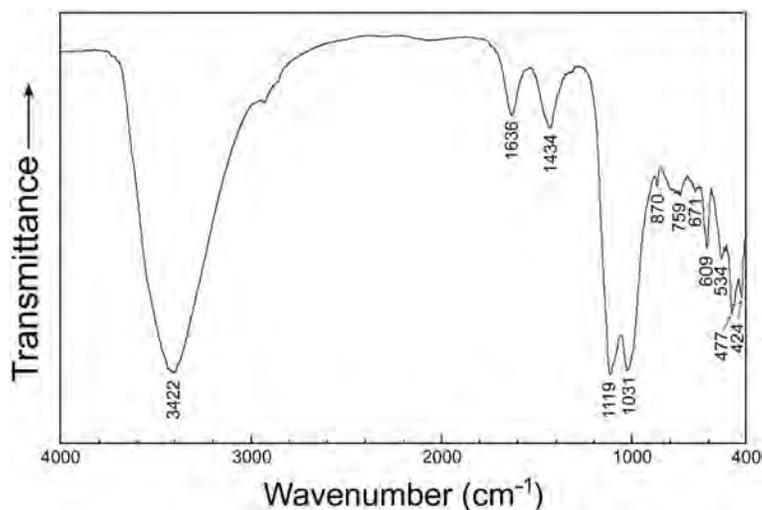
FIG. 4. FTIR spectrum of minohlite from the Hirao mine.

1636 cm^{-1} is attributed to the H–O–H bending vibration. The strong absorptions at around 1119 cm^{-1} and 1031 cm^{-1} are attributed to ν_3 and ν_1 SO$_4$ stretching vibrations, respectively, and those at around 609 cm^{-1} and 477 cm^{-1} are attributed to ν_4 SO$_4$ bending vibrations. A weak absorption band at 1434 cm^{-1} is due to the vibrations of the carbonate group derived from the smithsonite impurity.

Chemistry

Qualitative chemical analyses of minohlite using a scanning electron microscope (SEM) equipped with an energy-dispersive spectrometer revealed that the mineral consisted mainly of Cu, Zn and S, with small amounts of Fe and Si. Chemical zoning and intergrowth were not observed with back-scattered electron (BSE) imaging (Fig. 2b). Quantitative analyses of the mineral were carried out using a JEOL JXA-8105 electron microprobe analyser with wavelength-dispersive spectrometers at Kyoto University. Analysis conditions were an accelerating voltage of 15 kV, beam current of 4 nA, and beam diameter of 5 μm. The standard materials employed were cuprite (CuKα), sphalerite (ZnKα and SKα), hematite (FeKα) and quartz (SiKα). All the data were corrected with a ZAF method using a JEOL program. Although the H$_2$O content was not measured because of the small quantity of sample available, the presence of both O–H stretching and H–O–H bending vibrations was confirmed

by the FTIR spectrum as described above. Therefore, the H$_2$O content was calculated as being the difference between 100 wt.% and the weight percentage of the anhydrous components. As the (Cu + Zn + Fe):(S + Si) molar ratio of the mineral is close to 7:2, the empirical formula was calculated on the basis of Cu + Zn + Fe + S + Si = 9 atoms per formula unit (a.p.f.u.). The hydroxyl group was assumed to be present in a sufficient quantity to keep electrostatic charge balance. The empirical formula is (Cu$_{4.43}$Zn$_{2.45}$Fe$_{0.06}$)$_{\Sigma6.94}$ [(SO$_4$)$_{1.99}$(SiO$_4$)$_{0.07}$]$_{\Sigma2.06}$(OH)$_{9.64}$·7.81H$_2$O allowing for rounding errors, which leads to a simplified formula of (Cu,Zn)$_7$(SO$_4$)$_2$ (OH)$_{10}$·8H$_2$O. This formula, recalculated on the basis of 26 O a.p.f.u. and 10 (OH) + 8 (H$_2$O), can
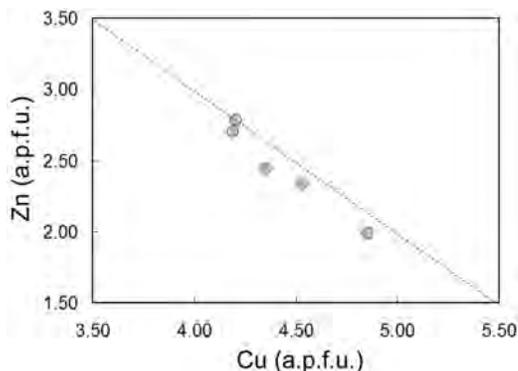
FIG. 5. Compositional variation in Cu *vs.* Zn in minohlite from the Hirao mine.

TABLE 2. Chemical composition of minohlite from the Hirao mine.

	1	2	3	4	5	— Average —	
Wt.%							
CuO	34.39	41.46	35.30	37.08	37.65	37.18	
ZnO	22.72	17.38	20.29	25.11	19.92	21.08	
FeO	0.37	0.67	0.44	0.45	0.50	0.49	
SO_3	16.46	16.65	16.97	16.86	16.98	16.78	
SiO_2	0.37	0.86	0.39	0.36	0.20	0.44	
H_2O						24.03*	24.80**
Total	74.31	77.02	73.39	79.86	75.25	100.00	100.77
Molar ratio (Cu+Zn+Fe+S+Si = 9 a.p.f.u.)							
Cu	4.19	4.85	4.35	4.21	4.53	4.43	4.41
Zn	2.71	1.99	2.45	2.78	2.34	2.45	2.45
Fe	0.05	0.09	0.06	0.06	0.07	0.06	0.06
S	1.99	1.94	2.08	1.90	2.03	1.99	1.98
Si	0.06	0.13	0.06	0.05	0.03	0.07	0.07
H						25.27	26.00

* With H_2O calculated by difference.
** With H_2O calculated on the basis of 10 (OH) + 8 (H_2O).

also be given as $(Cu_{4.41}Zn_{2.45}Fe_{0.06})_{\Sigma6.92}$ $[(S_{0.99}Si_{0.03})_{\Sigma1.02}O_4]_2(OH)_{10}\cdot8H_2O$. The results of chemical analyses are listed in Table 2. The compositional variation in Cu *vs*. Zn in minohlite from the Hirao mine shows an inverse correlation (Fig. 5). The range of Cu varies from 4.19 to 4.85 a.p.f.u., and Zn varies from 1.99 to 2.78 a.p.f.u.

Discussion

Minohlite has the simplified formula of $(Cu,Zn)_7(SO_4)_2(OH)_{10}\cdot8H_2O$ where Cu > Zn, and a hexagonal cell. The mineral is the 17th known Cu- and/or Zn-dominant basic sulfate mineral. The other 16 minerals are as follows: antlerite, bechererite, brochantite, christelite, kobyashevite, ktenasite, lahnsteinite, langite, montetrisaite, namuwite, osakaite, posnjakite, ramsbeckite, redgillite, schulenbergite, and wroewolfeite. Of these, schulenbergite $[(Cu,Zn)_7(SO_4)_2(OH)_{10}\cdot3H_2O]$ also has a (Cu + Zn):S ratio of 7:2; however, its crystallographic data are different from those of minohlite (Table 3).

The crystal structure of schulenbergite was reported by Mumme *et al*. (1994). The structure contains brucite-like layers of edge-sharing, predominantly CuO_6, octahedra oriented parallel to the (001) plane and connected to the corner of SO_4 tetrahedra. The unit-cell parameters of

schulenbergite are also reported by von Hodenberg *et al*. (1984), Mumme *et al*. (1994) and Ohnishi *et al*. (2007a, 2010). The *a* axis ($\approx$ 8.3 Å) of minohlite is similar to that of schulenbergite. The length of the minohlite *a* axis suggests that a building block of the structure is a $(Cu,Zn)_7(O,OH,H_2O)_{14}$ layer as found in schulenbergite. On the other hand, the *c* axis ($\approx$ 8.1 Å) of minohlite is longer than that of schulenbergite ($\approx$ 7.2 Å), presumably due to accommodation of the extra H_2O. The structural unit of minohlite is probably a basic building unit of $(Cu,Zn)_7(SO_4)_2(OH)_{10}(H_2O)_2$, with $6H_2O$ between layers. Minohlite can, therefore, be considered as a higher hydrated analogue of schulenbergite.

von Hodenberg *et al*. (1984) also reported an unknown '8.2 Å Phase' as an associated mineral of schulenbergite from Germany. The unit-cell parameters of this phase are *a* = 8.29 Å and *c* = 8.2 Å, and the morphological and chemical properties are similar to schulenbergite and namuwite. The details of other crystallographic data, chemical composition and physical properties of the phase were not given in the literature, but these lattice parameters of the phase are in close agreement with those of minohlite. The similarities of lattice parameters and chemical properties suggest that the '8.2 Å Phase' is identical to minohlite.

TABLE 3. Comparison of chemical formula, crystallographic data, and physical properties between minohlite and schulenbergite.

	Minohlite	Schulenbergite
Symplified formula	$(Cu,Zn)_7(SO_4)_2(OH)_{10} \cdot 8H_2O$	$(Cu,Zn)_7(SO_4)_2(OH)_{10} \cdot 3H_2O$
Crystal system	Hexagonal (or trigonal)	Trigonal
Possible space groups	$P6$, $P\bar{6}$, $P6/m$, $P622$, $P6mm$, $P\bar{6}2m$ and $P6/mmm$ ($P3$, $P\bar{3}$, $P321$, $P3m1$, $P\bar{3}m1$, $P312$, $P31m$ and $P\bar{3}1m$)	$P3$ or $P\bar{3}$
Unit-cell parameters		
a (Å)	8.2535(11)	8.211 to 8.256
c (Å)	8.1352(17)	7.106 to 7.207
V (Å^3)	479.93(16)	414.9 to 425.4
Z	1	1
Main powder X-ray diffraction pattern [$d_{meas.}$ in Å (I)]	8.138 (20)	7.186 (100)*
	4.128 (24)	3.581 (40)*
	2.702 (100)	3.209 (30)*
	2.564 (76)	2.700 (80)*
	1.560 (43)	2.527 (80)*
	1.532 (24)	2.157 (30)*
		1.559 (30)*
$D_{calc.}$ (g cm^{-3})	3.28	3.38 to 3.45
Colour	Bluish-green	Light blue green, greenish blue, blue green, pale green, emerald green
Lustre	Pearly to vitreous	Pearly, vitreous
Hardness (Mohs)	<2	1 to 2
Reference	Present work	* von Hodenberg *et al.* (1984); Mumme *et al.* (1994); Ohnishi *et al.* (2007a, 2010)

Acknowledgements

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