N. Jb. Miner. Mh. Jg. **1997** (4) 163–174 Stuttgart, Mai 1997

Donathite discredited: a mixture of two spinels

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With 3 figures and 4 tables in the text

BURNS, P. C., HAWTHORNE, F. C., LIBOWITZKY, E., BORDES, N. & EWING, R. C.: Donathite discredited: a mixture of two spinels. – N. Jb. Miner. Mh. **1997** (4): 163–174; Stuttgart (1997).

Abstract: Donathite from Ramberget (Hestmona), Norway, has been examined by Rietveld structure refinement, scanning electron microscopy and transmission electron microscopy. Testing of both single- and multi-phase models by Rietveld structure refinement gave the best fit to the pattern for a mixture of a cubic spinel (Fd3m, a = 8.3847(2) Å, $Fe^*_3O_4$; $Fe^* = Fe^{2+}+Fe^{3+}+Cr$) and a tetragonal spinel ($P4_122$, a = 5.2946(3), c = 8.3144(4), $Mg^*_{1.74}Fe^*_{1.26}O_4$, $Mg^* = Mg+Al$). These compositions were confirmed qualitatively by analytical electron microscopy. Leaching donathite results in a boxwork of lamellae of a cubic spinel of composition $(Mg_{0.53}Fe^{2+}_{0.43}Ti_{0.04})(Cr_{1.18}Fe^{3+}_{0.43}Al_{0.31}Fe^{2+}_{0.08})O_4$; the composition of this residual phase was modified by extensive chemical exchange with the acids used in the dissolution process. Donathite is a mixture of two phases, and its discreditation as a valid mineral species has been approved by the International Mineralogical Association Commission on New Minerals and Mineral Names.

Key words: Donathite, Rietveld structure refinement, electron microscopy, spinel, mixture.

Introduction

Donathite was formally described by SEELIGER & MÜCKE (1969) as a tetragonal spinel with a = 8.342, c = 8.305 Å, space group P4/nnm, although its existence as an anisotropic spinel has been well-known since the work of DONATH (1930). Donathite was considered to be a Zn-bearing solid solution of chromite and magnetite, the tetragonal structure resulting from the incorporation of Zn into the structure. MOORE (1977) showed that some samples

0028-3649/97/1997-0163 $ 3.00

of donathite were normal cubic spinels; one sample that could not be indexed on a cubic or a tetragonal cell, he proposed to be a mixture of one cubic and two tetragonal phases. LIBOWITZKY (1991) examined original material of SEELIGER & MÜCKE (1969), together with several other samples from Ramberget, Hestmona, and North Vaernes (both in northern Norway). He showed that donathite consists of a very fine lamellar intergrowth, with the lamellae of the minor phase too small to characterize by electron-microprobe analysis; however, the Zn content of the mixture was negligible (<0.1 wt % ZnO). LIBOWITZKY (1991) proposed that donathite is actually a mixture of magnetite and chromite, and that the anisotropic optical behaviour is due to form birefringence (WIENER 1912, 1926).

It is well-established that the anisotropic spinels from Hestmona consist of a mixture of oxide phases. However, the composition of the constituent phases has not been satisfactorily determined, and donathite has remained an accredited mineral species. Resolution of these two issues is the object of the current study. Discreditation of donathite as a valid mineral species has been approved by the International Mineralogical Association Commission on New Minerals and Mineral Names[1].

Experimental

The samples used are those of LIBOWITZKY (1991). X-ray intensity data were collected on a Siemens D-5000 X-ray powder diffractometer operating in transmission geometry. The sample was spread on a 4 µm-thick Prolene film with hairspray as the mounting medium; sample thickness is a critical parameter for transmission geometry, and the optimum sample thickness was derived by trial-and-error. An incident-beam monochromater was used to produce monochromatic CuKα_1 X-rays from a narrow-focus X-ray tube, in conjunction with a 2-mm antiscatter slit, a 0.1 mm receiving

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[1] The process of discreditation of a mineral follows this path:
1.) Evidence for discreditation is submitted to the relevant subcommittee of the CNMMN (Commission on New Minerals and Mineral Names) of the IMA, and the committee votes on the proposal. There is no one person associated with this process; it is approved by vote of the entire committee.
2.) If the vote is positive, the mineral is considered as discredited ONLY IF an article describing its discreditation is published within two years of the IMA vote. If the article is not published within this time, the vote of the CNMMN(IMA) lapses and the mineral remains accredited.

slit, and a Kevex solid-state detector. The sample was rotated at 120 rpm during data collection which extended over the range $15 \leq 2\theta \leq 120°$ using a 0.02° step-width and a 15 s count-time on each step.

The sample was dispersed in acetone, deposited on a Cu grid covered with holey carbon film, and examined using a JEOL 2000FX transmission electron microscope operating at 200 kV. A Tracor Northern TN-5500 energy-dispersive X-ray analysis system was used to qualitatively determine the compositions of the areas from which electron-diffraction patterns were obtained.

Approximately 1 g of sample was mixed with 10 ml 37 % HCl, warmed to 90 °C and left for 16 h with periodic shaking. The mixture was then centrifuged at 3000 rpm for 10 min, separating the residual powder from the orange-brown acid. These steps were repeated several times, and the final three cycles used distilled water instead of acid. This acid-leached material was attached to an acryl sample holder by liquid carbon. Since the sample was conducting, no carbon coating was applied. SEM images were obtained on a JEOL JSM-6400 scanning electron microscope at 10 kV using a sample distance of 14 mm. Quantitative analytical information was obtained with a LINK energy-dispersive X-ray system at 20 kV, using homogeneous chromite as a standard.

Rietveld structure-refinement

The Rietveld structure-refinement was done with the program DBWS-9006PC (SAKTHIVEL & YOUNG 1990) installed on an IBM RS-6000. Atomic scattering factors were taken from the International Tables for X-ray Crystallography (1974). Diffraction peaks were modelled using the Thompson-Cox-Hastings modified pseudo-Voigt profile-function, corrected for asymmetry up to 30° 2θ; the background was modelled using a refinable fifth-order polynomial. The occupancy of each cation site was considered as a refinable parameter. For the donathite sample, which previous work has indicated to be a mixture (LIBOWITZKY 1991), we proceeded in an ordered sequence of refinement steps that are summarized in Table 1. Refinement of a single cubic phase is obviously unsatisfactory both from the high R-indices and the presence of unaccounted peaks in the diffraction pattern, and the situation is not materially improved by refining a single tetragonal phase. Refinement of two cubic phases produces a significant improvement both in R(Bragg) for the major phase and in the various R(pattern)-indices;

however, the R(Bragg) index for the second cubic phase is very high at 15.3 %. Refining a cubic phase and a tetragonal phase produces a dramatic improvement in the R(Bragg) indices for both phases and in the various R(pattern) indices. Refinement of three cubic phases produced very low R(Bragg) indices for the two more abundant phases (Table 1) but a high R(Bragg) for the third phase, and a higher R(wp) for the overall pattern.

The results for the acid-leached sample are also summarized in Table 1. Refinement of a single cubic phase is relatively satisfactory; refinement of a single tetragonal phase produces no significant improvement in the fit to the powder pattern, and structural parameters converge to those obtained from the single cubic-phase refinement.

Results

Donathite

As shown in Table 1, Rietveld structure-refinement of the bulk material shows that donathite is a mixture of spinels. Examination of Table 1 shows that the best agreement was obtained for a mixture of one cubic spinel and one tetragonal spinel. The observed, calculated and difference powder patterns for this model are shown in Fig. 1. The difference pattern shows that there is no significant unaccounted diffraction intensity. There are small maxima and minima under each intense peak; this is the result of problems

Table 1. Comparison of Rietveld refinements for different structural models; R_B = (Bragg), R_P = R (pattern), R_{wP} = R (weighted pattern), R_{wP} (exp) = ideal R (weighted pattern) for this set of data.

Material	$R_B(1)$	$R_B(2)$	$R_B(3)$	R_P	R_{wP}	R_{wP}(exp)
			Original Donathite			
1 cubic phase	6.7	–	–	17.7	24.3	15.3
2 cubic phases	4.7	15.3	–	16.1	22.0	15.3
3 cubic phases	1.9	2.5	8.7	15.0	20.8	15.3
1 tetragonal phase	6.6	–	–	17.3	24.2	15.3
1 cubic, 1 tetragonal	3.3	6.6	–	13.8	19.5	15.3
			acid-leached sample			
1 cubic phase	6.0	–	–	14.8	21.3	16.0
1 tetragonal phase	5.9	–	–	14.6	21.2	16.0

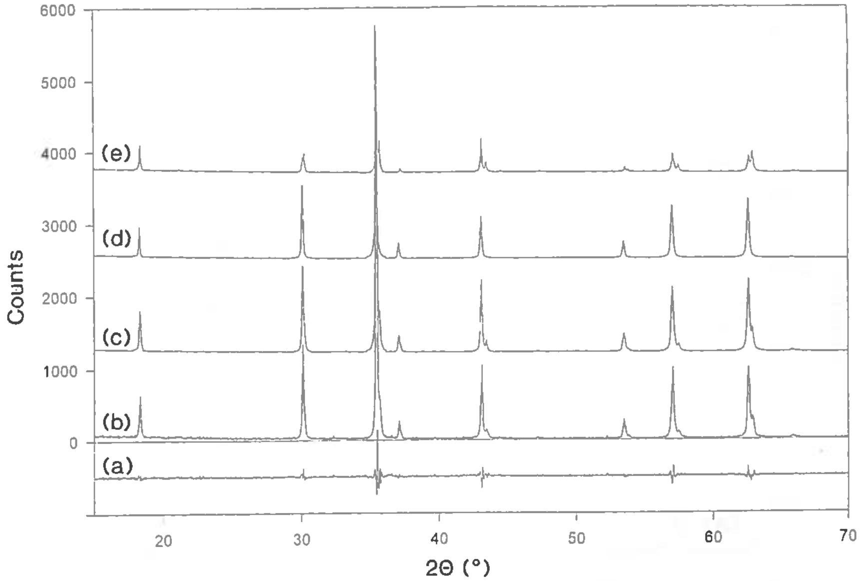

Fig. 1. Powder pattern of donathite for the Rietveld refinement of one cubic spinel and one tetragonal spinel; (a) the difference pattern (observed-calculated); (b) observed pattern; (c) total calculated pattern; (d) calculated pattern for the cubic spinel; (e) calculated pattern for the tetragonal spinel; the patterns are truncated at $2\theta = 70°$, although the refinement was done over the 2θ range 15–120°.

with the exact description of the peak shape. In a single-phase refinement, this does not introduce much inaccuracy into the structure model, as the structural parameters depend only on the total intensity under each peak; the peak-shape problems usually result in both positive and negative discrepancies under a single peak, and these tend to cancel out (Fig. 1 a). However, in a multiphase mixture, as is the case in the present refinement, peak-shape errors may lead to errors in the total intensities of overlapping peaks. However, the consistency of the refinement results with the chemical and microscopy results indicate that any such error is not adversely affecting the refinement results. The next-best-fit was obtained for a model consisting of a mixture of three cubic spinels. Careful examination of the observed and calculated diffraction patterns for both models (Fig. 2) shows that the model with three cubic spinels is not adequate. Fig. 2 a shows the observed diffraction pattern in the 2θ range 52–67°. The two strongest peaks at ~57° and

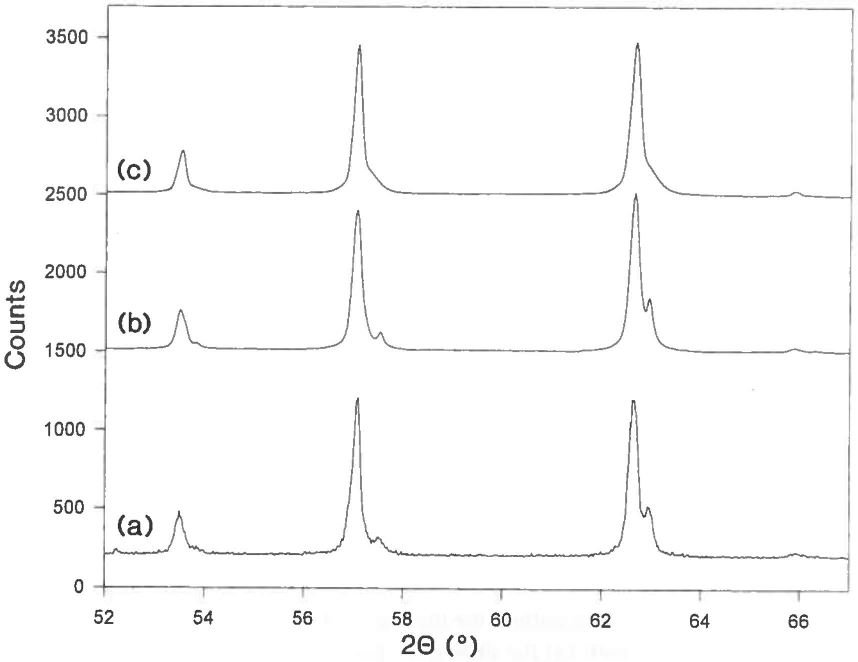

Fig. 2. Comparison of observed and calculated powder patterns for donathite over the range 2θ = 52–67°; (a) observed pattern; (b) calculated pattern for the refinement involving one cubic spinel and one tetragonal spinel; (c) calculated pattern for the refinement involving three cubic spinels.

~62.5° 2θ have prominent subsidiary maxima at slightly higher values of 2θ. The model consisting of one cubic spinel (Fig. 2 b) and one tetragonal spinel fits these subsidiary maxima very well. On the other hand, the model consisting of three cubic spinels does not fit these subsidiary maxima very well, merely giving subsidiary wings rather than discrete maxima.

The results for the best refinement are given in Table 2. The site-scattering refinement for the cubic phase indicates that the M sites are completely occupied by transition metals. The bulk composition of donathite (Table 3) shows only Fe and Cr (plus minor Mn) to be possible candidates; the fact that the refined scattering is ≥26e indicates that both M(1) and M(2) must be dominated by Fe in the cubic phase. The cubic phase is thus a Cr-bearing magnetite. The details of the tetragonal phase suggest that it does not contain Mn^{2+}, and thus the small amount of Mn in the bulk material (Table 4)

Table 2. Rietveld structure-refinement results for one cubic and one tetragonal phases for donathite.

	x	y	z	B (Å^2)	*S (e)
Phase 1:	cubic, Fd3m, a = 8.3847 (2) Å, ~65 % of mixture				
M(1)	1/8	1/8	1/8	0.5 (1)	27.5 (6)
M(2)	1/2	1/2	1/2	1.0 (1)	26.8 (6)
O(1)	0.2583 (7)	0.2583 (7)	0.2583 (7)	0.3 (1)	8
Phase 2:	tetragonal, $P4_122$, a = 5.9246 (3) c = 8.3144 (4), ~35 % of mixture				
M(1)	0.247 (2)	0.247 (2)	3/8	1.1 (3)	15.5 (6)
M(2)	0	0.255 (5)	0	0.4 (5)	17.4 (8)
M(3)	1/2	0.259 (6)	0	1.3 (5)	18.0 (7)
O(1)	−0.027 (4)	0.756 (7)	0.257 (3)	2.1 (8)	8
O(2)	0.497 (5)	0.265 (8)	0.232 (4)	3.9 (1.1)	8

* Effective scattering in electrons/site.

Table 3. Chemical analysis of donathite*.

TiO_2	0.66
Al_2O_3	4.4
Cr_2O_3	16.7
Fe_2O_3	50.0
FeO	22.0
MnO	0.36
MgO	4.9
	99.02

* From LIBOWITZKY (1991).

Table 4. Rietveld structure refinement results for leached donathite.

Cubic, Fd3m, a = 8.3474 (1) Å					
	x	y	z	B (Å^2)	S (epfu)
M (1)	1/8	1/8	1/8	0.89 (8)	18.2 (3)
M (2)	1/2	1/2	1/2	0.72 (5)	21.3 (3)
O (1)	0.2613 (4)	0.2613 (4)	0.2613 (4)	1.1 (2)	8

is assigned to the cubic phase. The site-scattering refinement for the tetragonal phase indicates that all of the lighter scatterers (Mg,Al) are completely ordered into this phase. From the refined site-scattering values, the site populations may be assigned in terms of (Mg,Al) and (Fe,Cr), giving a composition $(Mg,Al)_{1.74}(Cr,Fe)_{1.26}O_4$.

In the TEM, donathite shows strongly mottled diffraction contrast. The most abundant phase is cubic with a ~8.385 Å, and qualitative EDS analysis shows the presence of Fe and Cr only, with Fe>Cr. A second phase can be indexed on a tetragonal cell with a = 5.925, c = 8.314 Å, but the measured *d*-spacings are very similar to those of the dominant cubic phase. Qualitative EDS analysis shows the presence of Fe, Cr, Mg and Al in the tetragonal phase, in qualitative agreement with the results of the Rietveld structure refinement.

Leached donathite

Rietveld structure refinement of the leached material (Tables 1 and 4) shows no discernable deviation from cubic symmetry. However, comparison with the refined site-scattering values from the cubic+tetragonal spinel refinement (Table 2) shows that the leached phase does *not* correspond in composition to either the cubic or the tetragonal phase of untreated donathite. We may express the composition of the leached phase in terms of the joint scattering species (Al,Mg) and (Cr,Fe): $(Al,Mg)_{1.01}(Cr,Fe)_{1.99}O_4$.

The acid-leached material was examined in an SEM; typical images are shown in Fig. 3. At low magnification, the grains appear foliated, but higher-magnification images show a latticework of orthogonal lenses of material. Lamellar thickness varies in the range 30–500 nm, and resemble typical exsolution textures. Quantitative EDS analysis (on very uneven surfaces) gave the composition $(Mg_{0.53}Fe_{0.43}Ti_{0.04})(Cr_{1.18}Al_{0.31}Fe_{0.51})O_4$, in reasonable agreement with the composition determined by Rietveld site-scattering refinement.

Discussion

As has been shown by previous work, the original donathite sample is a mixture of two phases. The Rietveld results presented here show conclusively that the mixture consists of one cubic spinel phase of composition $(Fe^{2+},Mn)(Fe,Cr)_2O_4$ (a = 8.385 Å) and one tetragonal spinel phase of composition $(Mg,Al)_{1.74}(Cr,Fe)_{1.26}O_4$. Furthermore, the two phases are inter-

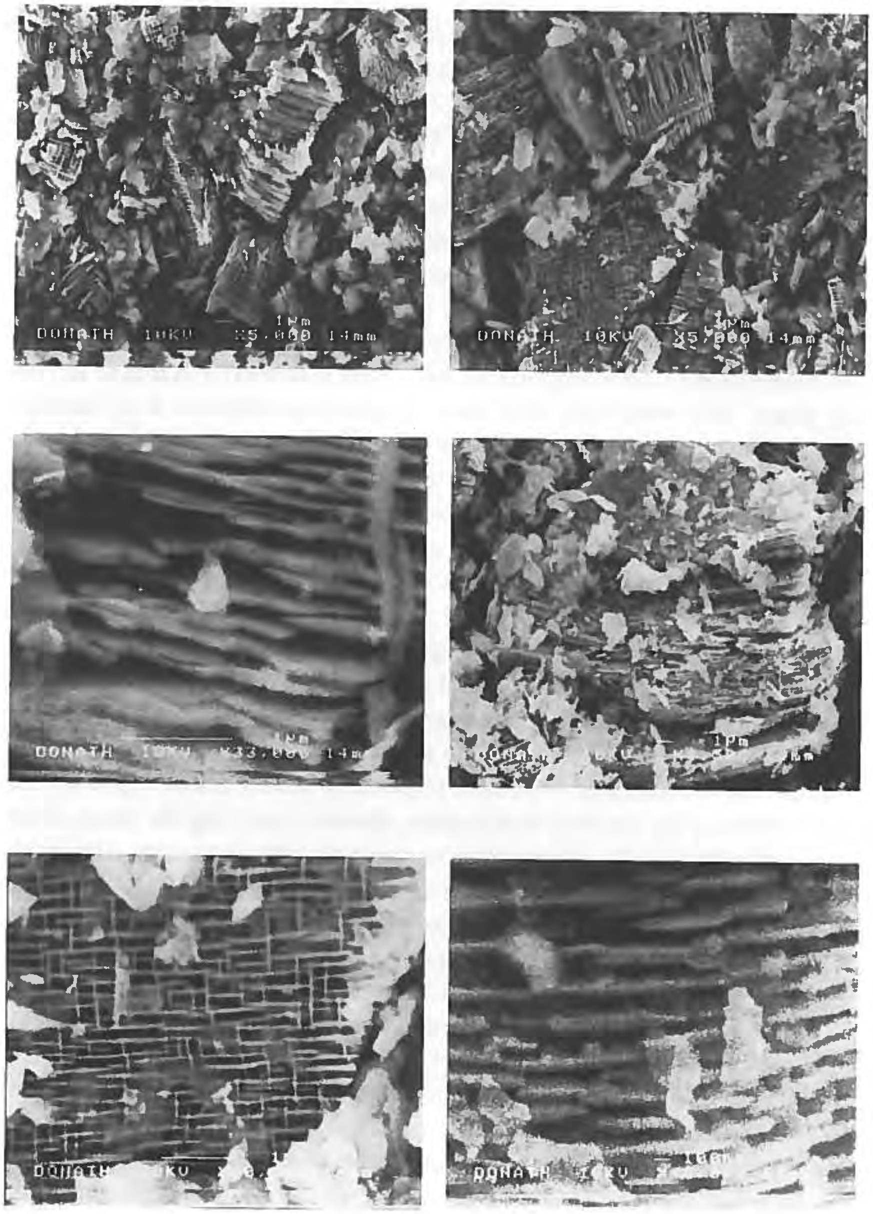

Fig. 3. Typical SEM images of leached donathite; note the foliated appearance at lower magnifications and the boxwork of lamellae visible at high magnifications.

grown in an oriented manner that suggests that the mixture formed by exsolution from a single homogeneous phase at higher temperatures.

We can use the scale factors from the Rietveld structure refinement, together with the compositions derived from the site-scattering refinement, to calculate the modal amounts of the two phases (HILL & HOWARD 1986). This procedure indicates that the donathite sample consists of 65 % (by weight) cubic phase and 35 % tetragonal phase. The site scattering refinement shows all Mg and Al to occur in the tetragonal phase. Using the bulk chemical composition of the mixture (Table 3), the Mg and Al contents of the tetragonal spinel may be calculated $Mg_{1.01}[Al_{0.073}(Cr,Fe)_{1.26}]O_4$. Thus the composition of the tetragonal phase is very different from that of the cubic phase. This means that they have significantly different X-ray absorption coefficients, and hence it is probable that the relative amounts of the two phases are inaccurate due to differential absorption of X-rays; this effect has been well documented by BISH & POST (1993). Given the composition of the tetragonal phase and the cubic phase [in terms of (Mg,Al) and (Fe,Cr)], we may calculate the relative proportions (wt %) from the analysis given in Table 3. This results in 78 % cubic phase and 22 % tetragonal phase (compared with ~65 % and ~35 % respectively by the Rietveld method).

Why is the (Mg,Al)-bearing spinel phase tetragonal? This is certainly not implicit in the chemical composition. We can only suggest that the tetragonal nature is a result of strain due to structural mismatch at the lamellae boundaries. We did hope to be able to confirm this by dissolving away the cubic phase in the leaching experiments, thereby removing the cause of the strain and allowing the minor phase to revert to cubic symmetry. The residual phase did have cubic symmetry after leaching, but it is also apparent that there was extensive chemical exchange between the minor phase and the acid solutions during the dissolution process, and we cannot use this result as a test of this idea.

The leached material appears optically anisotropic, showing distinct birefringence in cross-polarized light. The Rietveld structure refinement shows that the leached material is cubic. The optical anisotropy arises from *form birefringence*. As discussed by LIBOWITZKY (1991), form birefringence is the origin of the optical anisotropy of donathite. Removal of one of the phases in the lamellar intergrowth, and its concomitant replacement by air, produces a much greater refractive index contrast between the lamellae (i.e., leached donathite and air), and greatly enhances the form birefringence.

Conclusions

Donathite is a mixture of two spinel minerals and is discredited as a mineral species.

Acknowledgements

Financial assistance was provided by the Natural Sciences and Engineering Council of Canada in the form of Operating, Major Equipment and Infrastructure Grants to FCH, who was supported by a Killam Fellowship. The analytical electron microscopy was done at the Electron Microbeam Analysis Facility in the Department of Earth and Planetary Sciences, University of New Mexico.

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Accepted: November 14, 1996.