

# Iron-rich talc–opal–minnesotaite spherulites and crystallochemical relations of talc and minnesotaite

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## SYNOPSIS

ZONED spherulites in greenalite–siderite–silica rocks of the Emilia–San Valentin lead–zinc deposit, Sierra de Cartagena, SE Spain, show a core of iron-rich talc,  $(\text{Mg}_{1.8}\text{Fe}_{1.2})\text{Si}_4\text{O}_{10}(\text{OH})_2$ , an intermediate zone of opal-chalcedony, and a rim of minnesotaite,  $(\text{Fe}_{2.7}\text{Mg}_{0.3})\text{Si}_4\text{O}_{10}(\text{OH})_2$ . Crystallization of the spherulites, presumably from under-cooled silica sols carrying dissolved Mg and Fe, began with the non-equilibrium precipitation of metastable iron-rich talc; the residual fluids enveloping the growing spherulites became more iron-rich in composition until metastable equilibrium between iron-rich talc and iron-enriched

residual liquid impeded the further growth of the iron-rich talc; the spherulites were then overgrown by colloidal silica flocculates and a rim of minnesotaite precipitated from the iron-enriched residual fluid. The proposed crystallization model implies that, if talc and minnesotaite represent an isomorphic series, under equilibrium conditions there is a broad immiscibility region in the series.

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IRON-RICH TALC-OPAL-MINNESOTAITE SPHERULITES AND  
CRYSTALLOCHEMICAL RELATIONS OF TALC AND MINNESOTAITE

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The Emilia-San Valentin lead-zinc deposit, Sierra de Cartagena, SE Spain, was formed in relation to Tertiary rhyolitic volcanism by hydrothermal alteration of limestones into sulphide-carbonate-magnetite-greenalite-silica rocks. Four mineralization stages can be recognized, with progressive infiltration of metasomatizing solutions (Oen, *et al.*, 1975; Kager, 1980): (1) fracturing and dissolution of limestone; siderite fracture- and vug-fillings, and greenalite alterations along bedding, fractures, and siderite veinlets in the limestones; (2) fracture- and vug-fillings with siderite, galena, sphalerite, pyrite-marcoisite, and quartz-opal-chalcedony; formation of greenalite pods and masses impregnated with the same minerals as in the vugs; (3) abundant opal-chalcedony-quartz and Fe-Mn-Zn carbonates in fractures and vugs; recrystallization of greenalite masses into masses with greenalite, sulphides, magnetite, siderite, and opal-chalcedony-quartz; (4) youngest fractures and vugs with sulphides, opal-chalcedony-quartz, calcite, and dolomite. Mineralization occurred at low pressures, less than 300 m below the post-Miocene surface (Oen *et al.*, 1975); inferred maximum temperatures were about 250°C in mineralization stage (1), between 250°C and 400°C in stage (2), and about 300°-350°C in stages (3) and (4) (Kager, 1980).

In the stage (3) rocks containing greenalite,  $(\text{Fe}_{2.3}\text{Mg}_{0.7})\text{Si}_4\text{O}_{10}(\text{OH})_2$ , magnesian siderite (55-98 mol.%  $\text{FeCO}_3$ , 2-45 mol.%  $\text{MgCO}_3$ , 0-25 mol.%  $\text{CaCO}_3$ ), and quartz-opal-chalcedony, the siderite often appears corroded and partially replaced by opal-chalcedony and fascicular and spherulitic aggregates, up to about 2.5 mm across, of iron-rich talc,  $(\text{Mg}_{1.0}\text{Fe}_{1.2})\text{Si}_4\text{O}_{10}(\text{OH})_2$ . The latter mineral was described previously as Fe-talc (Friedrich, 1964) and as Mg-minnesotaite (Kager, 1980). A recent reinvestigation has revealed the frequent occurrence of iron-rich talc spherulites enclosed in a frame of colloform opal and composite, zoned spherulites consisting of an iron-rich talc core, an intermediate zone of opal and chalcedony, and a thin rim of minnesotaite,  $(\text{Fe}_{2.6}\text{Mg}_{0.3}\text{Mn}_{0.1})\text{Si}_4\text{O}_{10}(\text{OH})_2$ , (fig. 1).

Iron-rich talc is colourless,  $a = 1.569 \pm 0.004$ ,  $\gamma = 1.602 \pm 0.004$ ,  $-2V_a = 15-20^\circ$ . In comparison, minnesotaite shows a weak brownish tint, slightly higher refractive indices, and lower birefringence, but due to the fine grain measurements cannot be made.

Microprobe analyses were made with a Cambridge Instruments Co. fully-automated Mark 9 Microscan operated at acceleration potentials of 15 and 20 kV. Standards used were pure metals (Fe, Zn) and analysed diopside (Si, Ca), grossularite (Al), rhodonite (Mn), olivine (Mg), and albite (Na). Raw data were corrected for matrix effects with the Mark 9 on-line ZAF-correction programme. Representative analyses of iron-rich talc and minnesotaite are given in Table I. Chemical analysis of impure mineral concentrates indicates the absence of trivalent iron. For some analyses the atomic ratios calculated on the anhydrous base of 11 oxygen atoms fit the idealized formula  $(\text{Fe}_x\text{Mg}_y)\text{Si}_4\text{O}_{10}(\text{OH})_2$  (Table I, a). However, many analyses show  $\text{SiO}_2$  in excess of that required by the formula. Despite varying  $\text{SiO}_2$ , the analyses indicate constant Fe/(Fe+Mg) ratios of  $0.42 \pm 0.03$  for iron-rich talc (38 analyses) and of  $0.91 \pm 0.02$  for minnesotaite (12 analyses). The analyses apparently show contamination by opal-chalcedony.

TABLE I. Microprobe analyses of iron-rich talc (a, b) and minnesotaite (c); wt % oxides and atomic ratios on the anhydrous base of 11 oxygen atoms in the formula;  $\text{H}_2\text{O}$  calculated as difference between sum of metal oxides and 100.0 %.

	a		b		c	
$\text{SiO}_2$	56.00	4.002	61.40	4.204	52.30	4.137
$\text{Al}_2\text{O}_3$	0.09	0.004	0.05	0.002	0.07	0.003
FeO	19.56	1.169	18.68	1.070	35.85	2.376
MnO	0.15	0.009	0.09	0.005	1.31	0.088
ZnO	0.09	0.005	0.12	0.006	--	--
MgO	16.91	1.801	14.71	1.501	2.08	0.245
CaO	--	--	0.04	0.003	0.04	0.003
$\text{Na}_2\text{O}$	--	--	0.03	0.002	0.04	0.003
$\text{H}_2\text{O}$	7.20		4.88		8.31	
	100.00		100.00		100.00	

Calculated formula after correction for excess  $\text{SiO}_2$ :

- a.  $(\text{Mg}_{1.80}\text{Fe}_{1.11}\text{Mn}_{0.01}\text{Zn}_{0.01})\text{Si}_4\text{O}_{10}(\text{OH})_2$   
 b.  $(\text{Mg}_{1.74}\text{Fe}_{1.24}\text{Mn}_{0.01}\text{Zn}_{0.01})\text{Si}_4\text{O}_{10}(\text{OH})_2$   
 c.  $(\text{Fe}_{2.62}\text{Mg}_{0.28}\text{Mn}_{0.10})\text{Si}_4\text{O}_{10}(\text{OH})_2$

After correction for excess  $\text{SiO}_2$  a constant composition can be calculated of  $\text{Mg}_{1.77 \pm 0.04}\text{Fe}_{1.22 \pm 0.04}\text{Mn}_{0.006 \pm 0.003}\text{Zn}_{0.004 \pm 0.003}\text{Si}_4\text{O}_{10}(\text{OH})_2$  for iron-rich talc, and of  $(\text{Fe}_{2.63 \pm 0.02}\text{Mg}_{0.27 \pm 0.03}\text{Mn}_{0.10 \pm 0.02})\text{Si}_4\text{O}_{10}(\text{OH})_2$  for minnesotaite.

Table II lists the X-ray diffraction lines obtained with a Guinier camera from powdered mineral concentrates of iron-rich talc and with a Gandolfi camera from powders of minnesotaite that were drilled out under the microscope. The X-ray powder patterns agree well with the patterns of talc and minnesotaite, respectively, as given in the JCPDS (1980) Mineral Powder Diffraction File.

Experimental work in the system  $\text{Mg}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ - $\text{Fe}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$  (Forbes, 1969, 1971) indicates that between 680° and 430°C the Fe/(Fe+Mg) ratio of talc increases with decreasing temperature from 0.02 to 0.05. The maximum extent of iron solid solution in talc has not been determined at lower temperatures, but is suspected to be limited because of the rarity of iron-rich talc. On the other hand, microprobe work on minnesotaite from iron formations (Klein, 1974; Flöran and Paszke, 1975, 1978; Miyano, 1978) indicates an almost continuous range of Fe/(Fe+Mg) ratios between 1.00 and

Table II. X-ray powder data for iron-rich talc and minnesotaite;  $d$  measured ( $\lambda$ ), intensities I estimated.

Talc, JCPDS-file 19-770		Iron-rich talc Cartagena		Minnesotaite, Cartagena		Minnesotaite, JCPDS-file 17-506	
$d$	I	$d$	I	$d$	I	$d$	I
9.35	100	9.416	100	9.6	100	9.60	100
4.59	45	4.601	60	4.75	50	4.78	20
4.56	25						
4.53	12					4.58	10
				3.33	40	3.33	25
		3.12	40	3.129	30	3.17	50
				3.18	70	2.75	20
		2.635	18	2.648	20	2.65	20
		2.610	14				
		2.597	20	2.597	20		
		2.589	14				
		2.496	20	2.514	40	2.52	70
		2.479	30				
		2.464	14				
		2.457	10				
				2.39	20	2.399	20
						2.204	20
						2.105	10
						1.907	10
						1.818	10
1.731	10b	1.740	40			1.651	10
						1.606	20
						1.592	15
						1.563	20
1.529	55	1.531	80				
1.524	12b						
1.511	12	1.512	10				

0.15 (fig. 2). The composite spherulites described here suggest isothermal crystallization of talc and minnesotaite, implying a miscibility gap between the two minerals. The spherulitic habit and the association with colloform opal suggest crystallization from colloidal dispersions or sols under conditions of undercooling, supersaturation, and difficult nucleation, permitting the crystallization of metastable talc of much more iron-rich composition than the equilibrium composition at the temperature of crystallization.

Fig. 2 shows a model for the talc-minnesotaite join in the system  $\text{MgO}$ - $\text{FeO}$ - $\text{SiO}_2$ - $\text{H}_2\text{O}$ ; available evidence (Forbes, 1971) suggests maximum crystallization temperatures of minnesotaite between 300 and 400°C. At the end of mineralization stage (3), silica-rich sols were consolidating into colloform opal, while talc spherulites crystallized from the undercooled dispersing liquid, presumably an aqueous solution carrying dissolved Si, Mg, and Fe, of the sols. In fig. 2 a liquid L that is undercooled at temperature T may start crystallization with the non-equilibrium precipitation of metastable iron-rich talc  $t_m$ . Isothermal crystallization of  $t_m$  will shift the residual liquid towards more Fe-rich compositions, and, assuming that solute diffusion is limited or slow in relation to crystal growth rate, the growing spherulites  $t_m$  will become enveloped by residual liquid the composition of which is moving from L to  $L_r$ . When  $L_r$  is reached, metastable equilibrium between  $t_m$  and  $L_r$  will expand further growth of the spherulites, which may then become overgrown by colloidal silica flocculates, instantaneously followed by minnesotaite  $m_n$  crystallizing from  $L_r$ . The result is a zoned spherulite with a core of metastable iron-rich

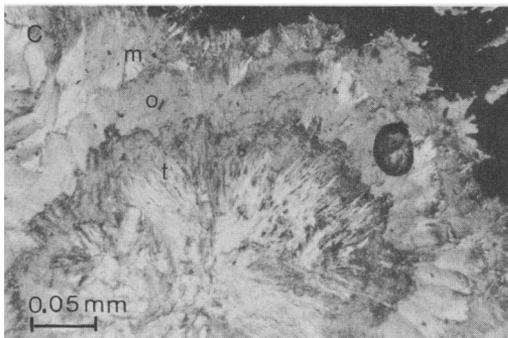
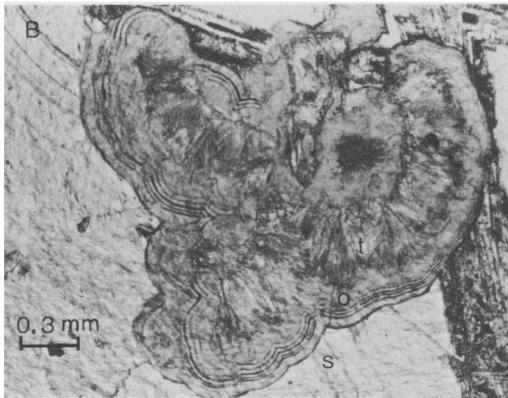
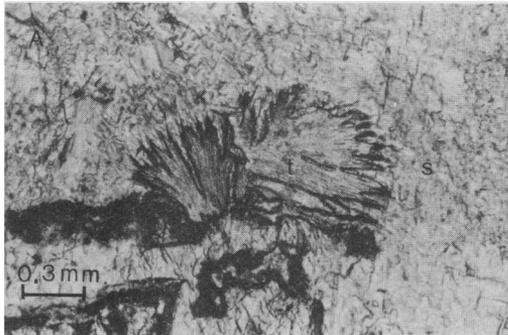


Fig. 1. A. Fascicular iron-rich talc (t) in magnesian siderite (s).  
B. Iron-rich talc spherulites framed in colloform opal-chalcedony (o).  
C. Zoned spherulite of iron-rich talc, opal-chalcedony and minnesotaite (m); black is galena.

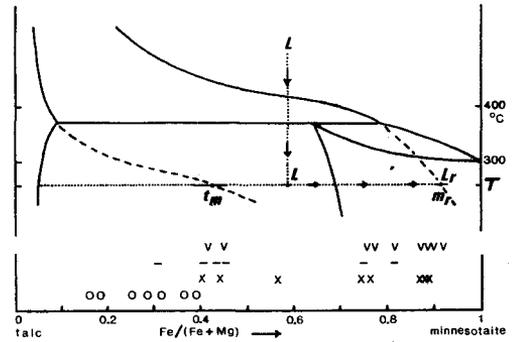


Fig. 2. Schematic diagram illustrating the phase relations along the talc-minnesotaite join and the crystallization of spherulites of iron-rich talc, opal, and minnesotaite as described in text. The lower part of the figure shows the compositions of minnesotaite from metamorphosed iron formations: (v) Klein (1974), (-) Floran and Papike (1975), (x) Floran and Papike (1978), and (o) Miyano (1978). Iron-rich talc and minnesotaite described in this paper are indicated by  $t_m$  and  $m_r$ , respectively.

talc  $t_m$ , an intermediate zone of opal, and a rim of minnesotaite  $m_r$ . The model in fig. 2 presumes that under equilibrium conditions there is a broad immiscibility region in the isomorphic series talc-minnesotaite and that iron-rich talc and magnesium-rich minnesotaite with  $Fe/(Fe+Mg)$  between about 0.1 and 0.7 can crystallize only as metastable phases under non-equilibrium conditions. Recent work (Guggenheim *et al.*, 1982) suggests that talc and minnesotaite may not represent an isomorphic series with identical structure and chemical formula. Fig. 2 may thus depict crystallization relations along a pseudo-binary rather than binary join.

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## REFERENCES

- Floran, R.J. and Papike, J.J. (1975). *Bull. Geol. Soc. Amer.* **86**, 1169-90.  
 --- (1978). *J. Petro.* **10**, 215-88.  
 Forbes, W.C. (1969). *Amer. Mineral.* **54**, 1399-408.  
 --- (1971). *J. Geol.* **54**, 63-74.  
 Friedrich, G. (1964). *Geol. Jahrb. Beiheft* **70**, 1-108.  
 Guggenheim, S., Bailey, S.W., Eggleton, R.A., and Wilkes, P. (1982). *Canad. Mineral.* **20**, 1-16.  
 JCPDS (Joint Committee on Powder Diffraction Standards) (1980). *Mineral Powder Diffraction File*.  
 Kager, P.C.A. (1980). Thesis, University of Amsterdam.  
 GUA-Papers of Geology (Amsterdam), Series I-12, 1-203.  
 Klein, C. (1974). *Canad. Mineral.* **12**, 425-96.  
 Miyano, T. (1978). *Geochem. J.* **12**, 201-11.  
 Oen, I.S., Fernández, J.C., and Manteca, J.I. (1975). *Econ. Geol.* **70**, 1259-78.