

SHOCK EFFECTS IN SCAPOLITE¹

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ABSTRACT

Shocked scapolite of the composition $\text{Mg}_{72-79}\text{Mg}_{21-23}$ occurs in the central, maskelynite bearing anorthosite massif of the Manicouagan-Mushalagan structure in Quebec, Canada. Highly shocked scapolite displays multiple sets of "planar features" identical to those reported in other shocked tectosilicates. Their crystallographic orientation was found to be parallel to the (100), (101), (102), (001) and (110) planes or their symmetrical equivalents. About 75 percent of the features are parallel to (100) and (001). No drastic changes in refractive indices (n_{α} : 1.588-1.586; n_{β} : 1.551-1.548) or X-ray unit cell dimensions ($a=b=12.11 \text{ \AA}$; $c=7.58 \text{ \AA}$) were found. Microprobe analyses of shocked and unshocked scapolite show no gross differences. Selective volatilization taking place at the 300-400 kbar shock level changes compositions marginally if at all; volatiles such as SO_2 are still present in the shocked material.

In comparison with other tectosilicates like quartz and feldspar, scapolite is remarkably resistant to shock damage, even at pressures probably exceeding 300 kbar. Some possible explanations of this abnormal behavior are discussed. The formation mechanism of planar features is reviewed, combining the results from scapolite, quartz and feldspar.

INTRODUCTION

Various minerals when subjected to the high pressures and strain rates of shock waves develop unique deformation features so far not observed in any endogenous or exogenous geological process but meteorite impact. The general trends of progressive shock deformation have been well documented and various stages of shock metamorphism can be established (Stöffler, 1966; Chao, 1967; Dence, 1968). Tectosilicates such as quartz and feldspar exhibit a variety of deformation features which are used as diagnostic criteria for the degree of shock damage. However, detailed knowledge of other mineral species is either scarce or completely missing. This paper describes some shock effects in scapolite from the central anorthosite of the Manicouagan-Mushalagan Lakes structure in Quebec, Canada (see also Dworak, 1969). This mineral was investigated, using standard universal stage, electron microprobe and Debye-Scherrer X-ray techniques.

SAMPLE DESCRIPTION

Figure 1 shows the general geological setting of the Manicouagan structure, as well as the locations of the anorthosites studied. The geology is discussed elsewhere (Murtaugh and Currie, 1969; Wolfe, 1966). Anorthosite from both inside and outside the structure is

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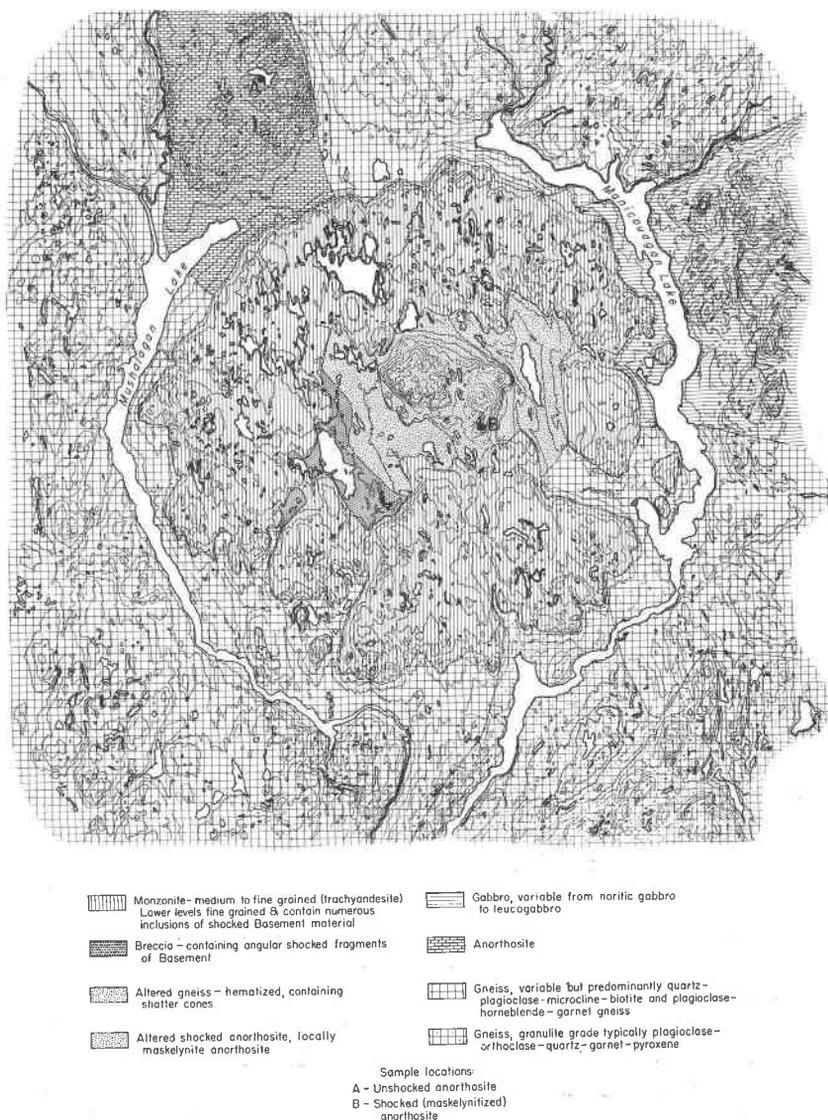


FIG. 1. Sketch map of the Manicouagan-Mushalagan structure, Quebec, Canada. (In part after Murtaugh and Currie, 1969).

about 85 percent plagioclase (An_{53-55}), the grains generally showing a bimodal size distribution with means about 0.5 and 1.5 mm. Larger grains are mostly albite and Carlsbad twinned. Clinopyroxene (approximately $Ca_{0.4}Fe_{0.2}Mg_{0.4}SiO_3$) is present in 1-mm grains which are often rimmed by subhedral or euhedral grains of garnet. Albitic and potassic feldspar is present in minor amounts as small, elongate grains along the edges of the plagioclase. Scapolite is a rather frequent accessory mineral with rounded, subhedral grains generally

0.5 to 1 mm in size. Apatite, as well as some hornblende and biotite are present in minor amounts.

Anorthosite inside the crater shows all stages of shock metamorphism from the merely fractured to the shock-melted stage. In a few localities in the central anorthosite massif, the material is strikingly altered (Wolfe, 1966), and about 99 percent of the plagioclase has been transformed to a water-clear glass of high refractive index, *i.e.* maskelynite (Tschermak, 1872; Duke, 1968), "diaplectic" feldspar glass (v. Engelhardt *et al.*, 1967), or "thetomorphic" feldspar (Chao, 1967). This Manicouagan material has been described by Bunch *et al.*, (1967).

OPTICAL STUDIES

About 50 percent of the scapolite which occurs in the isotropic material from the center of the structure exhibits closely spaced sets of planar features resembling those known from shocked quartz and feldspars. This scapolite is optically very uniform with no evidence of reduced

TABLE 1. REFRACTIVE INDICES AND CELL PARAMETERS OF SHOCKED AND UNSHOCKED SCAPOLITE

	Refractive Index		Bire-	$a = b$	c	$2\theta_{400} - 2\theta_{112}$ (deg.)
	$N_{\alpha} \pm .002$	N_{β}	fringence ΔN			
Unshocked I	1.588	1.551	.037	{ 12.111(40) 7.581(24) }	3.500	
Unshocked II	1.589	1.551	.038			
Shocked I	1.586	1.550	.036	{ 12.157(05) 7.563(24) }	3.400	
Shocked II	1.587	1.548	.039			

birefringence or extensive fracturing, although undulous extinction is sometimes observed. For the most part, scapolite both inside and outside the crater appears nearly identical. Measurements of refractive indices obtained on isolated grains with immersion techniques are listed in Table 1. An appreciable amount of scapolite in the central anorthosite exhibits sets of planar features. One and two sets occur frequently (both shocked grains used for index determination displayed two sets of planar features), while grains with three sets are rare. These features (see Fig. 2) are identical to "planar features" (Carter, 1968), "planar elements" (v. Engelhardt and Bertsch, 1969), or "shock lamellae" (Chao, 1967). They are of the undecorated type. As in quartz and feldspar (see French and Short, 1968; Stöfler, 1967), most of the measured inclinations of planar feature poles to the optic (c -axis) in scapolite coincide with angles of rational crystallographic planes (Fig. 3). The majority of planar features in scapolite occur along planes of the general crystallographic form $\{001\}$, $\{102\}$, $\{101\}$ and $\{100\}$.

In order to identify the specific crystallographic directions of these features, inclination measurements and angular relations in the azimuth

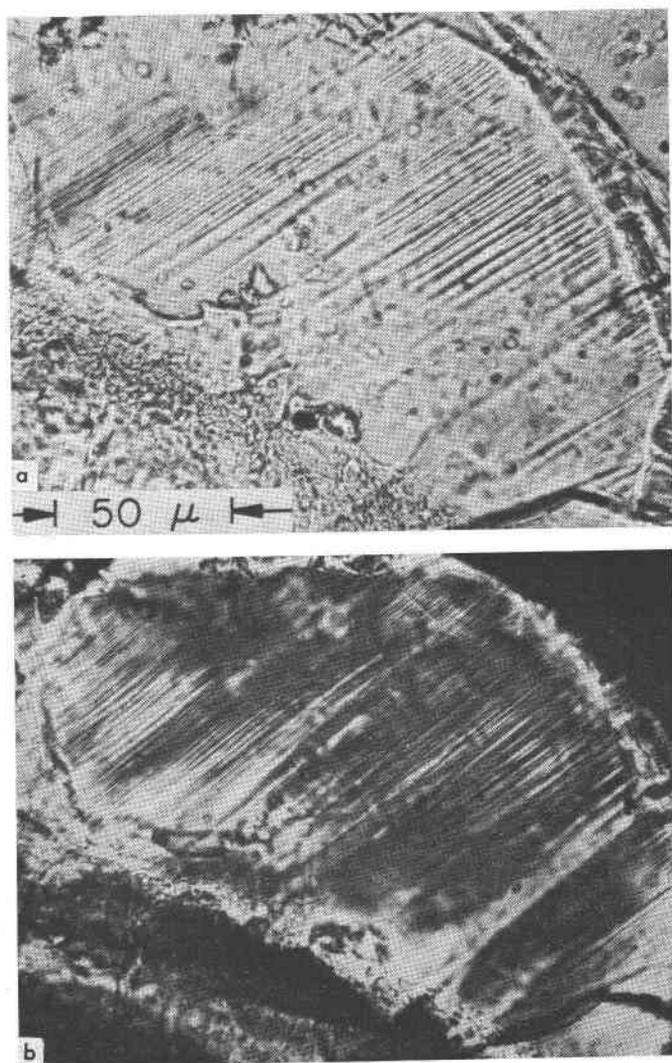


FIG. 2. Planar features in scapolite: a) plane light; b) crossed nicols.

plane have been plotted on a stereonet for grains with two or three sets of planar features (Fig. 4), (about 65 percent of all the measured grains). Grains showing only one set of features were omitted, since their azimuth values are ambiguous. Plots for grains with two or three sets of planar features retain the angular relations between the measured elements. Unfortunately, these scapolites displayed no prominent cleavage which would have allowed orienting each individual stereoplot with the (100) pole (the prominent cleavage direction of scapolite). We, therefore,

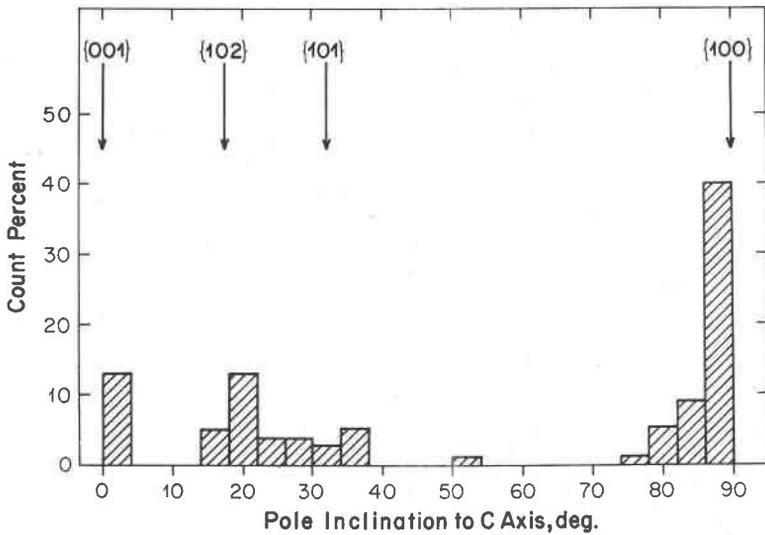


FIG. 3. Angles between optic axis and poles of planar features in scapolite (79 measurements in 46 grains).

arbitrarily decided to have at least one of the measured features coincide with the [010] zone; the measured inclinations to the optical axis suggested preference of the [010] zone over the [110] zone.

Accordingly, we could demonstrate (see Fig. 3) that planar features in scapolite are parallel to the planes (100), (101), (102), (001) or their symmetrically equivalent forms. The only features parallel to planes of the [110] zone seem to be of the type (110). Table 2 shows the absolute and relative frequencies of planar features using the data reduction scheme of v. Engelhardt *et al.* (1968).

CHEMICAL COMPOSITION

Chemical compositions of coexisting scapolite and plagioclase in both shocked and unshocked anorthosite were determined using an ARL-EMX electron microprobe. Both phases were analyzed in each of three shocked and two unshocked rocks. For samples #41-#44, three scapolite and two to three plagioclase grains were analyzed, while for samples #48 and #50 only one grain of each phase was run. Each analysis consists of data averages from approximately six $20\mu\text{m}^2$ areas of the grain; mineral standards were used and oxide contents were determined (for SO_3 anhydrite with 58.81 percent SO_3 was the standard used). Data obtained, after correcting for background and deadtime, were reduced to oxide contents using the procedure of Bence and Albee (1968).

The averages of the grains analyzed in each sample are shown in Table

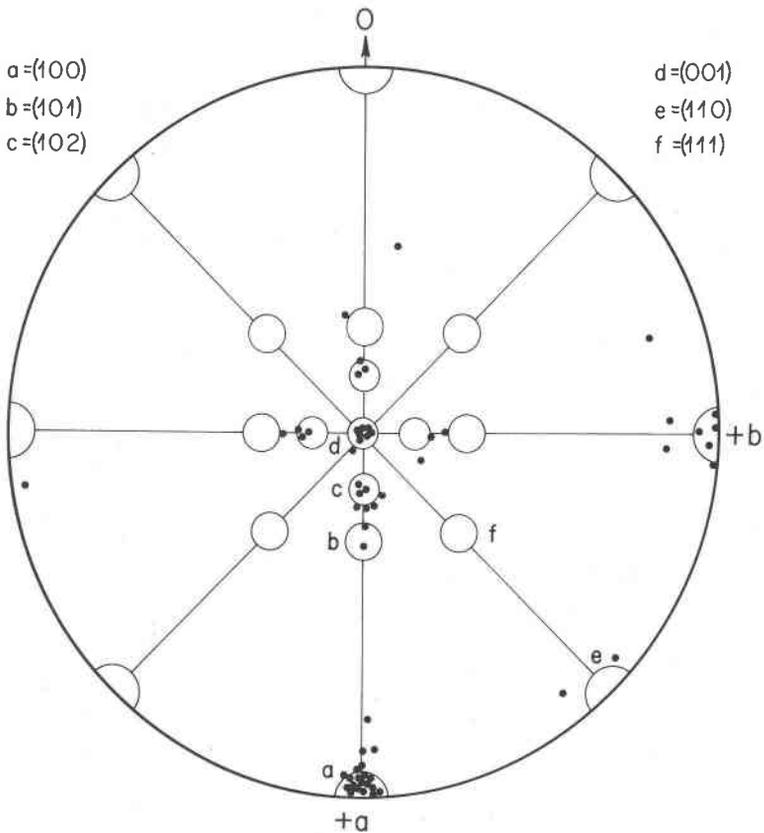


FIG. 4. Stereoplotted poles of scapolite with planar features (only grains with two or three sets are plotted).

3, as well as standard deviations (in percent) calculated from the observed variations among grains in the same sample. The scapolite data are also shown in terms of the normalization: $\text{Si} + \text{Al} = 12.00$ atoms, as suggested by Evans *et al.* (1969). The number of Ca, Si, $\text{Ca} + \text{Na} + \text{K}$ ($= \sum \text{W site}$) and S atoms, as well as the meionite contents are also shown. These values are averages of values observed for grains in the same sample. The CO_2 values shown are not measured, but they are estimated from the stoichiometry proposed by Evans *et al.* (1969) [$\text{C} + \text{S} = (\text{Ca} + \text{Sr})/3$]. This procedure is used in order to estimate the total oxide content, exclusive of H_2O ; water contents of from 0 to 1.3 percent are indicated. The analyses indicate a value of Me_{72-77} which is in good agreement with the refractive indices and the $2\theta_{400} - 2\theta_{112}$ calculated from the Debye-Scherrer patterns (see Table 1).

These analyses, with the exception of #41, #48, and the low sulfur

TABLE 2. FREQUENCIES OF PLANAR FEATURES IN SCAPOLITE^a

	A	B	C	D	E
{100}	135	35	50.0	25.9	36.5
{101}	140	8	11.4	5.7	7.9
{102}	140	17	24.3	12.1	17.1
(001)	34	9	12.9	26.5	37.4
{110}	136	1	1.4	.7	1.0
		70	100.0	70.9	99.9

^a For data reduction scheme see v. Engelhardt *et al.* (1968)

A = No. of observable planes after correcting for blind circle of universal stage.

B = No. of actually observed planar features.

C = $(B/\Sigma B) \cdot 100$ = Apparent frequency.

D = $(B/A) \cdot 100$ = Unnormalized probability.

E = $(D/\Sigma D) \cdot 100$ = True frequency or probability.

areas of #50, are in good agreement with the stoichiometry of Evans *et al.* (1969); #48 and #41 show somewhat lower W site summations than those normally observed by Evans (3.92-4.06), but #50 is quite anomalous.

Sample #50 is an anorthosite which appears to have been more severely shocked, or at least to have attained a higher temperature, than either #41 or #44. It was analyzed to check for selective volatilization at higher shock intensities. The plagioclase appears to have melted and produced a thermal glass along the grain boundaries, and the plagioclase grains themselves display anomalous optical characteristics with $2V$ ranging from 30 to 0 degrees (cf. normal An_{55} has $2V \sim 80^\circ$). The garnets in this sample are very heterogeneous with localized concentrations of Fe, Ca, Mg and Al on a 20 μm to 50 μm scale. The scapolite grains are also heterogeneous with areas 10 μm to 40 μm in dimension containing 7.5 percent SO_3 ("high S" areas in Table 3), while other parts of the grain ("low S" areas) have non-detectable SO_3 concentrations. This heterogeneity in the scapolite and garnet is not observed in the unshocked anorthosites or in the maskelynitized samples (#41, #44 and #48). The high sulfur areas of the scapolite in #50 conform well to the stoichiometric relations but the low sulfur areas do not; it is not clear what these low sulfur areas are, and they may represent some intermediate breakdown stage of scapolite.

Sample #48 is cut from a chip adjacent to #41 and was analyzed to see if the anomalies in #41 are real; they appear to be.

From this data it is evident that the compositions of plagioclase and scapolite, in both the maskelynitized and unshocked anorthosites, are

TABLE 3. MICROPROBE ANALYSES OF MANICOUAGAN SCAPOLITES AND PLAGIOCLASES (OXIDES AS WT. %)

Scapolite								
Sample	Shocked					Unshocked		
	#44	#41	#48	#50 High S Low S		#43	#42	Std. Dev. (percent)
SiO ₂	44.9	45.4	45.5	45.3	51.9	45.1	45.3	2
Al ₂ O ₃	26.8	27.2	27.6	26.0	29.2	26.1	26.6	2
Na ₂ O	3.30	2.57	3.04	3.52	3.12	3.66	3.33	5
K ₂ O	0.15	0.15	0.15	0.16	0.13	0.10	0.20	8
CaO	17.7	18.2	17.5	17.2	14.8	17.1	17.3	2
SO ₃	4.04	2.67	2.71	7.52	0.0	6.61	3.45	5
Tot.	96.9	96.2	96.5	99.7	99.2	98.7	96.2	
CO ₂ †	2.5	2.8	2.8	0.0	—	1.0	2.5	
Σ Oxides —H ₂ O	99.4	99.0	99.3	99.7	99.2	99.7	98.7	
Σ W site	4.01	3.80	3.81	4.02	3.07	4.06	3.95	
Ca	2.98	3.00	2.88	2.91	2.21	2.91	2.90	
S	.48	.31	.31	.89	0	.77	.40	
Si	7.04	7.04	7.00	7.15	7.21	7.14	7.09	
% Me	74.2	78.9	75.5	72.3	71.9	71.5	73.4	
Plagioclase								
Sample	Shocked				Unshocked			
	#44	#41	#48	#50	#43	#42	Std. Dev. (percent)	
SiO ₂	53.6	54.6	55.2	55.2	55.6	55.0	3	
Al ₂ O ₃	28.8	28.4	28.2	28.4	27.0	27.6	5	
Na ₂ O	4.51	4.79	5.07	5.12	5.56	5.09	6	
K ₂ O	0.55	0.52	0.60	0.52	0.33	0.37	15	
CaO	11.5	11.3	10.7	10.7	10.7	10.9	5	
Tot.	99.0	99.6	99.8	99.9	99.2	99.0		
% An.	56.6	54.1	52.0	51.9	50.5	53.0		

† CO₂ values are estimated from the scapolite stoichiometry proposed by Evans *et al.* (1969).

not grossly different and, in fact, are quite similar. The differences that exist do not appear to be systematic. The lower Na_2O and SO_3 contents of #41, compared to #42 and #43, might be attributed to some process of selective volatilization, but the K_2O content is not lower, and the scapolite SO_3 content in #44, which is similarly shocked, is higher than in #42. In #50, both Na_2O and K_2O contents are similar to the unshocked rocks, and heterogeneities in SO_3 content rather than general volatile losses are observed.

A more likely interpretation of the data would be that the composition of phases in both the shocked and unshocked rocks are roughly similar and that the variations observed are mainly due *not* to the shock metamorphism but to preexisting variations in the anorthosite massif. Any selective volatilization at shock intensities which produce maskelnite has, at most, marginal effects on chemical composition. Production of heterogeneous phases seems to occur before systematic volatile loss takes place.

Experimentally produced shock waves of 300–450 kbar amplitude are known to produce isotropic feldspar phases (Milton and DeCarli, 1963). Neither the short “in-shock” temperature pulse of 400–500°C (Ahrens *et al.*, 1969), nor the residual temperature of the material ($\approx 100^\circ\text{C}$) is sufficient to selectively alter the composition of these minerals (see, also, Duke, 1968).

CELL PARAMETERS AND OTHER X-RAY DATA

Scapolite grains were picked from shocked and unshocked anorthosite and crushed to a fine powder. X-ray patterns were obtained using $\text{CuK}\alpha$ radiation in a 114-mm camera. These photographs are shown in Figure 5. It can be seen that shocked and unshocked material appear quite similar except for the absence of high-angle “back” reflections in the shocked material. The weakening or disappearance of back reflections is observed in cold-worked metals (Cullity, 1959), as well as in shocked quartz (Chao, 1968; Dachille *et al.*, 1968; Bunch, 1968) as a result of destruction of the crystal's long-range order. The cell parameters for both the shocked and unshocked materials are given in Table 1. The values are near those reported for the meionite end member of the series and, as such, agree with other parameters observed for this material.

DISCUSSION AND CONCLUSIONS

As has been mentioned earlier, anorthosite inside and outside the crater is believed to have formed at the same time and to have been shock metamorphosed at a later time. Scapolite is probably primary,

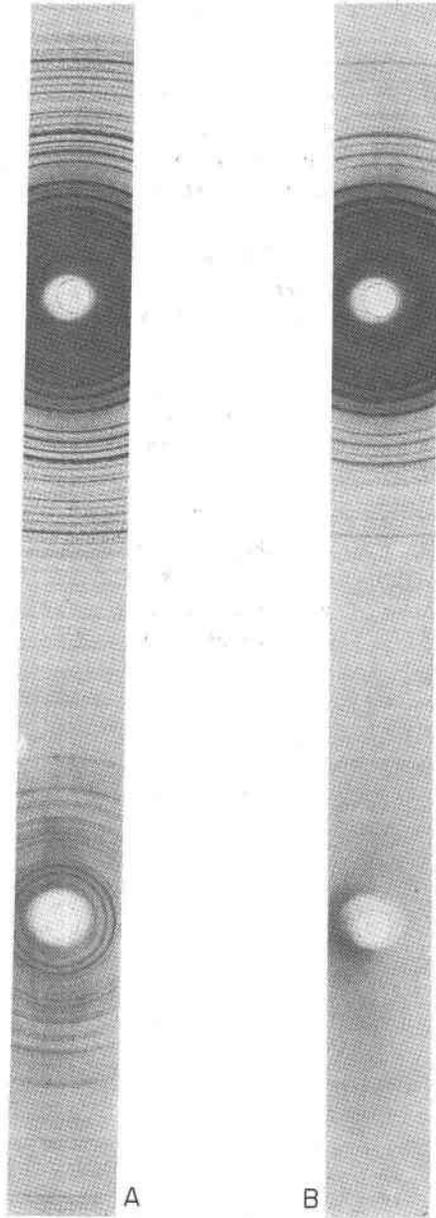


FIG. 5. Debye-Scherrer powder patterns of shocked and unshocked scapolite:
a) unshocked; b) shocked.

having been formed during the Grenville metamorphism and was present previous to the shock event.

The presence of planar features in the plagioclase and pyroxenes, and the presence of diaplectic feldspar phases (v. Engelhardt, 1967), is felt to be convincing evidence that the anorthosite within the structure has been shock metamorphosed. The closely spaced planar features in scapolite are identical to those reported from other silicates, the shock origin of which has been demonstrated in the laboratory by Short (1968), Müller and Defourneaux (1968) and Hörz (1968).

Recovery shock experiments by Milton and DeCarli (1963) on feldspar (250–350 kbar) and equation of state data of Ahrens *et al.* (1969) indicate that diaplectic feldspar glasses form in response to shock pressures in the range of 300–400 kbar. Ahrens *et al.* give 300 kbar as the lower limit for the formation of diaplectic glasses and 450 kbar as the pressure at which melting begins. Genuine melting was not observed in samples #41, #44 or #48. These data and the highly fractured condition of the coexisting pyroxenes (Carter, Raleigh and DeCarli, 1968) indicate that the anorthosite was probably shocked to about 400 kbar. Compared to plagioclase, which is completely transformed to diaplectic glass at these pressures, scapolite shows only minor shock damage. This is quite surprising; one might expect it to show similar behavior since scapolite and plagioclase have many structural similarities.

Both tectosilicates are composed of tetrahedra of four coordinated Al and Si atoms. If scapolite is viewed along the *c*-axis and plagioclase along a direction parallel to the *a*-axis, they are both seen to consist of stacks of four-membered rings of AlO_4 and SiO_4 tetrahedra which are linked in directions perpendicular to the stacking axes. The Ca, Na and K ions are located approximately on planes which run parallel to the stacking axes and between adjacent rows of stacks. When viewed in these directions, scapolite displays its fourfold rotation axis, and plagioclase is seen to have very nearly tetragonal symmetry. The main difference between the two structures is that in scapolite alternate stacks of rings are found to consist of only one-half as many four-membered rings in the stack. The resulting cavities in these stacks are filled with ions such as Cl^- , F^- , CO_3^{2-} , SO_4^{2-} (Papike and Stephenson, 1966; Papike and Zoltai, 1965; and Deer *et al.*, 1963). In contrast to plagioclase, shocked scapolite in Manicouagan anorthosite is not vitreous and shows essentially unchanged cell parameters, indices of refraction, birefringence and chemical composition. As far as can be ascertained, the only changes that took place during shock deformation were development of planar features and erasure of the back reflections in the Debye-Scherrer powder patterns.

Three possible explanations for this apparent anomaly are:

1) There might be a gross shock (acoustical) impedance mismatch between scapolite and plagioclase such that scapolite actually experienced much lower shock pressures than did the enveloping plagioclase.

2) It is possible that scapolite is more resistant to shock deformation than is plagioclase, with the ionic sublattice acting as a "stabilizer".

3) The presence of ionic bonds (*i.e.* Ca—CO₃ or Na—Cl) in scapolite tends to make the mineral behave in a plastic fashion. These bonds would ease gliding and increase recrystallization rates, thus preventing total lattice breakdown.

In view of the underlying structural similarities of scapolite and plagioclase and the small density differences (about 2%), the first explanation seems unlikely, but it cannot be discarded until elastic constants and equation of state data for scapolite are known. These data are not presently available. Structural similarities and similar hardnesses seem

TABLE 4. FREQUENCIES (COUNT %) OF PLANAR FEATURES IN GRAINS DISPLAYING ONE, TWO, OR THREE SETS OF PLANAR FEATURES

	No. grains	Crystallographic orientations					Irrational
		{100}	{101}	{102}	(001)	{110}	
1 set	17	71	6	23	0	0	0
2 sets	25	36	12	18	14	2	18
3 sets	4	50	8	25	17	0	0

to exclude large strength differences between the two, an indication that the second suggestion is unlikely as well. Due to the lack of more information about scapolite, the last explanation seems most likely at the present.

It has been shown (Müller and Defourneaux, 1968; Robertson, *et al.*, 1968; Hörz, 1968) that quartz develops differing sets of planar features with differing shock pressures. The data for scapolites, presented here, suggest that this mineral may also show such behavior. If the reasonable assumption is made that in a given rock progressively fewer grains experience shock pressures of increasing intensity, then the data of Table 4 suggest that as scapolite undergoes progressively higher shock pressures, planes with face poles at lower inclinations to the *c*-axis become populated with planar features, *i.e.* (101) and (102). This behavior is similar to that observed in quartz. If scapolite were an abundant rock-forming mineral, it might conceivably be used to establish a shock metamorphic subclass in the 300 to 400 kbar range with planes parallel to (100) appearing first, followed by a variety of other planes.

The data in Table 5 for scapolite, plagioclase and quartz strongly suggest that there is a basic difference between the formation mechanisms of

TABLE 5. CLEAVAGES, PLANAR FEATURES, AND Si-O BOND DENSITIES FOR SCAPOLITE, PLAGIOCLASE AND QUARTZ.

	Plane	Cleavage	Planar features percent		Si-O bonds/ 100 Å ²	
			(Data from this paper)			
Scapolite ^a	(100)	Excellent	34		3.01	
	(110)	Good	1		4.26	
	(001)	None	38		5.44	
	(101)	None	10		4.62	
	(102)	None	16		5.23	
			(Data from Stöffler 1967)			
Plagioclase ^a	(100)	None	10		6.62	
	(010)	Good	11		3.84	
	(001)	Perfect	25		3.82	
	(120)	None	10		4.35	
	(110)	Poor	0		3.85	
			A B			
			A B			
Quartz ^b	(0001)	37	26	31	22	9.60
	(10 $\bar{1}$ 0)	4	—	2	—	7.55
	(10 $\bar{1}$ 2)	5	2	14	15	8.15
	(10 $\bar{1}$ 3)	3	2	38	44	8.90
	(10 $\bar{1}$ 1)	19	47	6	5	5.90

A = Data from Hörz (1968).

B = Data from Robertson *et al.* (1968).^a Cleavages are normal (static) cleavages.^b Cleavages are shock induced.

cleavage and planar features. Various authors (Carter, 1968; v. Engelhardt and Bertsch, 1969) have discussed the optical characteristics which distinguish these two types of planar elements. In scapolite it is observed that cleavage takes place along planes with low numbers of Si-O bonds per unit area. Planar features, on the other hand, occur frequently along planes with high Si-O bond densities. This behavior is similar to that observed in plagioclase (Stöffler, 1967) and quartz (Robertson, *et al.*, 1968; Hörz, 1968). Table 5 lists the relative tendencies for formation of frequently observed cleavages and planar features in scapolite, plagioclase and quartz, and bond densities along the planes involved.

Some authors have suggested that slip or glide mechanisms are responsible for the formation of planar features (Chao, 1968; Carter, 1968; v. Engelhardt and Bertsch, 1969). This theory is compatible with the

experiments of Hörz (1968) and Müller and Defourneaux (1968) who found that in quartz, planar features form only under shock pressures of amplitudes greater than 120 kbar. Therefore, their formation occurs outside the elastic region of quartz (Hugoniot Elastic Limit $\sim 100-110$ kbar, Wackerle, 1962). This hypothesis is supported by the observation that for silicates, planes with high Si-O bond densities are, in general, planes along which the lattice repeat distance is the shortest, and in analogy with metals, slip would be expected to occur in these directions.

In accordance with this hypothesis, and on the basis of their optical investigations, v. Engelhardt and Bertsch (1969) have suggested that planar features are the traces of high pressure phases which nucleate, preferably along these planes, due to the increased dislocation densities caused by the gliding process. These high-pressure polymorphs convert, upon pressure release, partially or completely to disordered phases (Müller, 1969; Hörz, 1968).

According to the data in Table 5, some other mode of formation seems probable. Since planes with high bond densities are also the planes with the highest densities of silicon and oxygen atoms, they would be logical nucleation sites for high-pressure polymorphs. Such planes might also show short-range order analogies to the dense phases. The data of Ahrens *et al.* (1969) indicate that a phase change takes place in quartz at approximately 120 kbar, *i.e.* just slightly above the Hugoniot Elastic Limit. This is also in agreement with the observed minimum pressures for the planar feature formation. According to this hypothesis, compression only without gliding is required for the formation of high-pressure phases.

On the basis of the existing data, it is difficult to say which, if either, of these two hypotheses is correct. Both lead to high-pressure polymorphs along crystallographic planes which, upon pressure release, relax to highly disordered phases.

SUMMARY

Planar features observed in scapolite of the Manicouagan-Mushalagan anorthosite are oriented principally along symmetrical equivalents of the planes (100), (001), (102) and (101) in that order of frequency. Shocked scapolite is chemically very similar to unshocked scapolite and shows very little structural damage. Scapolite in shocked rocks might conceivably be used to define a shock metamorphic subclass in the 300-400 kbar range.

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