

## Djurleite from Calabona, Sardinia

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**SUMMARY.** Djurleite has been identified by X-ray analysis in a sample from Calabona, Sardinia. Morphological characteristics, chemical composition, and thermal behaviour (studied by high temperature X-ray analysis and D.T.A.) are reported. Chemical composition and breakdown products upon heating differ from those of synthetic djurleite in the Cu-S system.

**RIASSUNTO.** In un campione proveniente dalla miniera di Calabona, Sardegna, è stata identificata la djurleite. Vengono date le caratteristiche morfologiche, la composizione chimica e il comportamento termico, studiato mediante analisi a raggi X ad alta temperatura e A.T.D. La composizione chimica e i prodotti di decomposizione termica differiscono da quelli della djurleite sintetica riportati in letteratura.

DJURLEITE was discovered as a mineral by Roseboom (1962) and by Morimoto (1962) independently, in many specimens from different localities. Both these authors suggested that djurleite might be a common mineral, but since then only a few occurrences have been reported in the literature (Skinner, White, Rose, and Mays, 1967; Takeda, Donnay, Roseboom, and Appleman, 1967; Sillitoe and Clark, 1969; Morimoto, Koto, and Shimazaki, 1969; Clark and Sillitoe, 1971). Only Takeda *et al.* (1967) have recorded the presence of idiomorphic twinned crystals in a specimen from Neudorf, Germany.

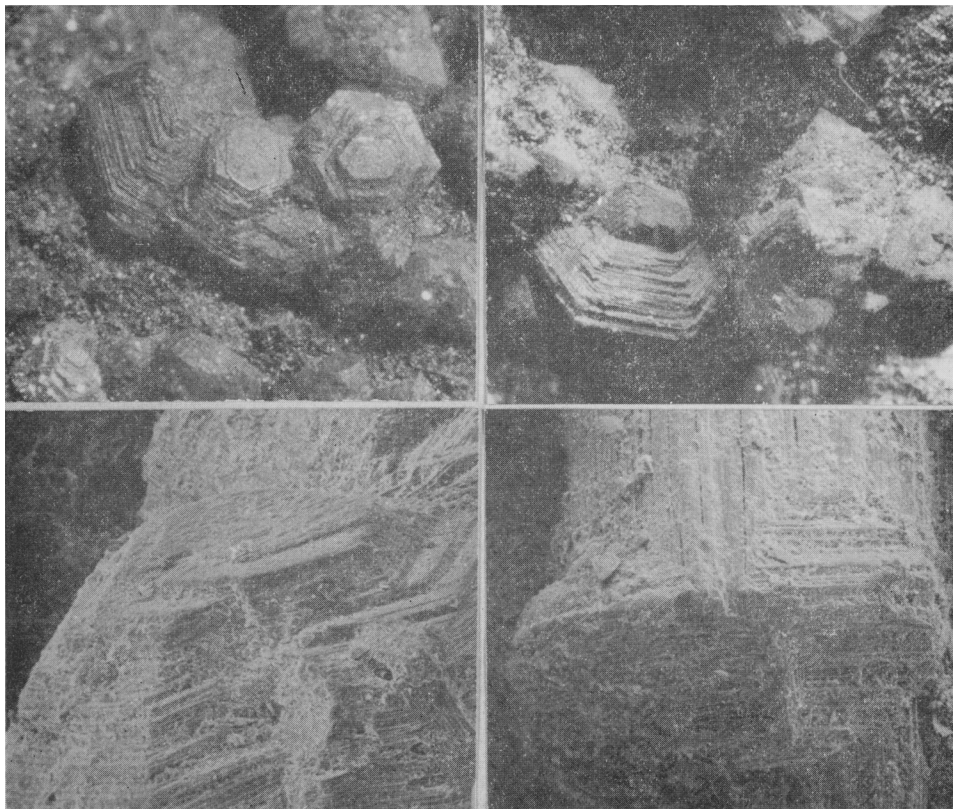
On the surface of a specimen from Calabona, near Alghero, Sardinia (n. 14003/66 of the Mineralogical Museum of the University of Florence), collected by Ciampi (1921), composed of pyrite, bornite, chalcocopyrite, covellite, luzonite, and famatinite, several crystals of djurleite have been identified. The pseudo-hexagonal djurleite crystals, which frequently show a short prismatic or truncated bipyramidal habit, have a laminated appearance (fig. 1a, b). These 'crystals' occasionally occur as penetration twins, which show a fourfold symmetry in a section perpendicular to the hexagonal surfaces (fig. 2a, b). Both the pseudo-hexagonal and the less common pseudo-tetragonal symmetries are consistent with the twinning theory given by Takeda, Donnay, and Appleman (1967).

As noted by Roseboom (1962), djurleite crystals in reflected light show colours, anisotropy, and hardness similar to those of chalcocopyrite. Polysynthetic twinning, as suggested by the striated crystal faces, has been detected.

The X-ray powder diffraction data of djurleite crystals from Calabona, recorded with a G.E. diffractometer X-RD 5, Cu-K $\alpha$  radiation with Ni filter, and silicon ( $a = 5.4283$  Å) as internal standard, match perfectly those obtained by Takeda, Donnay, Roseboom, and Appleman (1967) on a djurleite sample from Butte,

Montana. The data were averaged from two patterns run at  $\frac{1}{2}$  degree  $2\theta$  per minute, and the intensities were measured as relative peak heights on a strip chart.

To obtain further data on the djurleite crystals from Calabona, electron-probe and thermal analyses were performed. Two microscopically homogeneous djurleite crystals



FIGS. 1-2: FIG. 1a (top left). Macrophotograph of djurleite idiomorphic crystals with evident pseudo-hexagonal symmetry;  $\times 20$ . FIG. 2a (top right). Macrophotograph of djurleite penetration twins;  $\times 20$ . FIG. 1b (bottom left). Scanning electron micrograph showing laminated morphology;  $\times 70$ . FIG. 2b (bottom right). Scanning electron micrograph showing the pseudo-tetragonal symmetry;  $\times 100$ .

were analysed on a Philips Norelco Microprobe AMR/3, with acceleration voltage of 20 kV for S and 30 kV for Cu and Fe, using covelline from Calabona and metallic Fe as standards. The average of two analyses on each crystal, corrected for dead-time, background, mass-absorption, atomic-number, and characteristic-fluorescence effects using a computer program modified from Springer (1967), are compared with the analyses of synthetic Cu-rich digenite and of djurleite (Roseboom, 1966).

While the Cu content is in good agreement with the synthetic product, the S content is high and close to that of digenite. Therefore our recalculated formula, on the basis of  $S = 1$ , would be:  $\text{Cu}_{1.827}\text{Fe}_{0.0007}\text{S}$ .

X-ray diffraction patterns at high temperature were obtained with a 90 mm diameter Rigaku Denki camera using sealed silica-glass capillaries and silicon as external standard. The data recorded at temperatures of 190 °C and 460 °C are reported in table I. Both diffraction patterns show the presence of a single phase identified as high-digenite (Djurle, 1958; Morimoto and Kullerud, 1963; Roseboom, 1966).

	Djurleite (Calabona)	Digenite Cu <sub>1.79</sub> S	Djurleite Cu <sub>1.96</sub> S
Cu	79.7 %	78.02 %	79.54 %
Fe	0.03	—	—
S	22.0	21.98	20.46
	101.73		

D.T.A. experiments, performed using evacuated silica-glass containers, to a maximum temperature of 500 °C, show no thermal effect other than a small endothermic peak at 100 ± 3 °C. In table I the X-ray powder diffraction data taken on the sample

TABLE I. X-ray powder data for djurleite at various temperatures

hkl	Calabona				d	I/I <sub>0</sub>	d	I/I <sub>0</sub>	d	I/I <sub>0</sub>			
	1. 190 °C		2. 460 °C								3. Calabona	4. Tetragonal phase	5. Digenite
	d	I	d	I							d	I/I <sub>0</sub>	d
111	3.223	w	3.254	w	3.762	15	3.78	2	—	—			
200	2.7925	m	2.8125	m	3.255	23	3.27	7	—	—			
220	1.9826	vs	1.9965	vs	3.209	35	—	—	3.21	40			
311	1.6935	s	1.7058	s	—	—	—	—	3.05	10			
222	—	—	—	—	2.8248	24	{ 2.84	4	—	—			
400	1.4009	vw	—	—	—	—	{ 2.81	1	—	—			
422	1.1469	w	1.1579	vw	2.7828	41	—	—	2.79	40			
511	0.9521	vw	0.9595	vw	2.7395	88	2.749	10	—	—			
333					2.5488	15	—	—	2.53	5			
					2.3830	19	—	—	2.40	5			
					2.3007	71	2.307	9	—	—			
					2.2608	26	2.258	5	—	—			
					—	—	—	—	2.17	10			
					1.9959	56	2.003	9	—	—			
					1.9658	100	1.967	8	1.973	100			
					1.8860	25	1.889	7	—	—			
					1.8732	23	—	—	1.877	5			
					—	—	—	—	1.781	5			
					1.7648	11	1.769	3	—	—			
					1.7017	26	{ 1.706	8	—	—			
					—	—	{ 1.700	3	—	—			
					1.6790	21	—	—	1.686	30			
					1.6189	12	1.616	2	—	—			
					1.4892	11	1.494	1	—	—			
					1.4023	43	1.402	5	—	—			
					—	—	—	—	1.395	10			

1. Calabona at 190 °C. 2. Calabona at 460 °C. 3. Calabona at 25 °C after D.T.A. at 500 °C.  
4. Tetragonal phase (Skinner, 1970). 5. Digenite (A.S.T.M. 9-64).

after D.T.A. study are compared with the X-ray data of the tetragonal metastable phase (Skinner, 1970) and of digenite (A.S.T.M. n. 9-64).

The high-temperature X-ray analyses are in agreement with the phase relations studied by Roseboom (1966) (fig. 3), inasmuch as, according to this author, for all

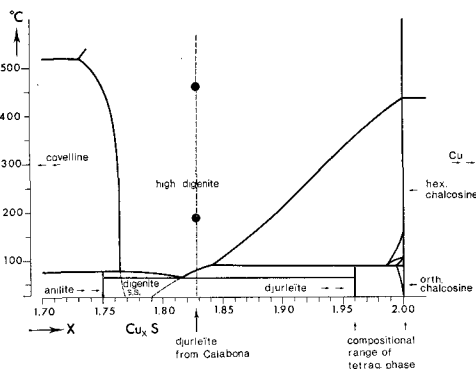


FIG. 3. Phase relations of Cu-S system by Roseboom (1966) and Morimoto and Koto (1970). Solid circles indicate the phase relations at 190 °C and 460 °C for djurleite from Calabona.

material of bulk composition  $\text{Cu}_x\text{S}$  with  $1.76 \leq x \leq 1.89$  at 190 °C and 460 °C only high-digenite should appear. On the other hand, the temperature of the endothermic peak at 100 °C for djurleite, obtained in this work, is too high not only in comparison with Roseboom's temperature of 93 °C obtained on an X-ray heating stage, but also with Graziani's (1965) temperature in his D.T.A. study. Finally, according to Roseboom, X-ray analyses after D.T.A. ought to show the presence of djurleite in addition to digenite and to the tetragonal phase.

Both the indication of the chemical composition ( $\text{Cu}_{1.827}\text{Fe}_{0.0007}\text{S}$ ) and the thermal behaviour of our sample are consistent with the possible existence of a djurleite with a Cu:S ratio lower than the theoretical  $\text{Cu}_{1.96}\text{S}$ . This might be caused by the presence of Fe traces, and the uncertainty of corrections taken for the S content in the microprobe analysis may in part explain such a Cu-poor formula. A more detailed laboratory investigation of djurleite stability in the Cu-Fe-S system as well as a larger series of chemical analyses on natural djurleite may clarify these problems.

According to Roseboom (1966) the occurrence of djurleite in single crystals is evidence of direct crystallization at temperatures below 93 °C. This conclusion is in agreement not only with the textural characteristics of our specimen, but also with the description of the Calabona mine given by Ciampi (1921), which indicates the zone of supergene sulphide enrichment, mainly mineralized by 'chalcosine', covellite, and pyrite, as the one exploited.

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