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JACOBSITE FROM THE NEGEV, ISRAEL

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The specimen of jacobsite investigated is the first reported occurrence from Israel and the middle east. The sample was not found in situ but obtained from a large boulder (approximately 1 cubic meter) which was mined from the vicinity of "manganese hill," 26 miles North of Eilat, in the Southern Negev (Sturm 1953 and Bentor 1956). All subsequent analyses were performed on a "fist-sized" sample removed from this boulder.

Physical Properties and Composition

In appearance, the specimen was predominantly of a deep black color, exhibiting a brownish-black streak test. It was very magnetic, being able to support a 3 inch alnico horse-shoe magnet with 1 cm² pole pieces. The hardness on the Mohs scale was just below 6 of feldspar. It was quite difficult to cut the specimen with a carborundum saw and sections were made using a diamond saw. No regular cleavage was observed and only an irregular fracture was obtainable.

Spectrochemical analysis indicated iron and manganese to be the major elements present plus small amounts of silicon, aluminium, barium and traces of other elements. Wet chemical analysis gave a content of:

29.0% manganese by weight
14.6% iron by weight

Polished Surface Studies*

The specimen is of complex mineralogy, very fine grained, considerably oxidized, and in general, a particularly difficult problem for mineralogical study. Fig. 1. is a photomicrograph made under low magnification. The very bright small particles (low left center) are hematite. The smooth fairly bright areas are jacobsite; the brightness varies as it is oxidized and hydrated to limonite, which most of the darker areas represent. In addition to jacobsite and hematite, several other phases are discernible. A

* Study performed by Dr. C. Milton of the U. S. Geological Survey, Washington 25, D. C.

Fig. 1. Photomicrograph (ordinary light). The very bright small particles (lower left center) are hematite. The smooth fairly bright areas are jacobsite; the brightness varies as it is oxidized and hydrated to limonite, which most of the darker areas represent. ×45

large part of the specimen appears to be hydrous iron oxide, goethite, as indicated by red internal reflections, low reflectivity and a considerable water content by closed tube test. There are veinlets cutting the specimen, apparently psilomelane or a similar manganese oxide.

X-RAY STUDY

When one considers the variety of oxidation states possible in iron and manganese ores, unambiguous identification of the phases present can best be accomplished by x-ray diffraction techniques. Debye-Scherrer photographs were taken from a region of the specimen which was found, by probing with a bar magnet, to be most magnetic. The polished surface study was made on a sample adjacent to this region. In Table 1 the powder diffraction data of the sample is presented with the identification of the various phases detected. There are two major phases present; α-Fe_2O_3 and jacobsite, a cubic phase which readily indexed as the spinel structure type. Trace amounts of goethite, α-$Fe_2O_3 \cdot H_2O$ and a calcium manganese oxide hydrate (ASTM 4-0149) were found. After a magnetic separation of the powdered sample was made, the non-magnetic fraction indicated the possible presence of bementite, $8MnO \cdot 7SiO_2 \cdot 5H_2O$. The 7.17 Å line has not been identified.

Table 1. *X*-ray Powder Data for Negev Ore

Fe/Mn filter, Fe K = 1.9373; Camera diameter 114.59 mm.

$d_{obs}(Å)$	I	Spinel phase (hkl)	$a_0(Å)$	$d_{obs}(Å)$	I	hkl	$a_0(Å)$
				(H) 1.631	M −	$\begin{Bmatrix}333\\511\end{Bmatrix}$	8.475
* 7.17	M			(H) 1.606	M −		
4.85	W	111	8.402	1.503	M +	440	8.502
(G) 4.25	VW			(H) 1.482	M		
(H) 3.625	M −			(H) 1.450	M		
2.982	M	220	8.433	1.345	W +	620	8.507
* 2.782	W			* 1.322	W +		
(H, G) 2.672	S			(H) 1.294	VW	533	8.485
2.547	M +	311	8.448	1.282	W	622	8.504
(H) 2.504	M +			(H) 1.257	W		
(G) 2.445	W +	222	8.469	(H) 1.227	VW	444	8.501
* 2.353	W			(H) 1.214	VW	$\begin{Bmatrix}711\\551\end{Bmatrix}$	8.491
(H) 2.195	M −			(H) 1.189	W		
2.113	M −	400	8.452	(H) 1.160	W		
(H) 2.079	VW			(H) 1.140	W	642	8.531
1.947	W +	331	8.487	* 1.118	W		
* 1.899	VW			1.107	VW	731	8.503
(H) 1.833	M			(H) 1.102	M		
1.728	W	422	8.465	1.065	W (Br.)	800	8.520
(H) 1.687	M +			(H) 1.055	W		
* 1.667	W						

G = goethite.

H = hematite.

* Unidentified.

The lattice constant of the spinel phase was determined by extrapolating the plot of the observed lattice constants for each (*hkl*) reflection against the Nelson and Riley (1945) function

$$\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$$

and found to be 8.51 ± 0.01 Å.

Discussion

At this point it is most appropriate to review the considerable discrepancies reported in the literature relative to the nomenclature, chemical composition, and lattice constants of the intermediate compounds belonging to the system whose end members are the cubic spinel, magnetite (Fe_3O_4), and tetragonal hausmannite (Mn_3O_4). Mason (1947) showed

that there was a complete range of solid solutions between Fe_3O_4 and Mn_3O_4 above 1200° C; exhibiting a cubic structure at room temperature from 0 to 60 mol per cent Mn_3O_4 and a tetragonal structure from 60–100 mol per cent Mn_3O_4. The unit cell dimension of the cubic phase increased with the mol per cent of Mn_3O_4 and the c/a ratio of the tetragonal phase increased from 1.00 to 1.16 above 60 mol per cent Mn_3O_4. From the study of some mineral specimens belonging to the system Fe_3O_4–Mn_3O_4, Mason found the evidence that compositions from approximately 54 to 91% Mn_3O_4 will form two phases if allowed to reach equilibrium; one cubic and one tetragonal. This was demonstrated by the mineral vredenbergite (an intergrowth of jacobsite and hausmannite). More recently Van Hook & Keith (1958) have verified Mason's findings and have investigated and characterized more completely the system Fe_3O_4–Mn_3O_4. They have shown that below 1160° C. there is a "progressively widening region of solid immiscibility in which a cubic phase and a tetragonal phase can co-exist in equilibrium." Their data corroborates Mason's results on natural intergrowths in the region 54 to 91% Mn_3O_4. They have suggested that Mason's nomenclature and subdivisions in the system Fe_3O_4–Mn_3O_4 be continued:

Mineral name	*Mol per cent Mn_3O_4*
magnetite	0– 10
jacobsite (magnetite-high hausmannite solid solution)	10– 54
vredenbergite (intergrowths of jacobsite and low hausmannite)	54– 91
hausmannite (low)	91–100

The increase in lattice constant for the cubic spinel phase with increasing content of Mn_3O_4 as reported by both Mason and Van Hook & Keith was found to follow an almost linear relationship. Although no single crystalline $(Fe,Mn)_3O_4$ phase with from 54 to 91% Mn_3O_4 is stable at room temperature, Van Hook & Keith obtained solid solutions in that compositional range only by quenching from higher temperature. Such cubic solid solutions are metastable at room temperature. This, of course, precludes their existence in minerals.

While it would be completely probable to find jacobsite with a lattice constant consistent with the appropriate amount of Mn_3O_4 in the compositional range 10–54 mol % Mn_3O_4 (Mason page 437), the synthetic manganese ferrite or $.33\ Mn_3O_4$–$.66\ Fe_3O_4$ would be expected to have one discrete unit cell dimension. This lattice constant would further depend on the ratio of Mn^{+2} and Mn^{+3} present and their relative occurrence on the A and B spinel sublattice sites. In Table 2 the reported lattice constants for jacobsite are compared with those of synthetic manganese ferrite. Among the synthetic manganese ferrites there is very good agree-

TABLE 2. REPORTED LATTICE CONSTANTS FOR JACOBSITE AND
SYNTHETIC MANGANESE FERRITE

Specimen	Mn_3O_4 content (mol per cent)	Lattice constant Å	Source	Reference
Jacobsite	? %	8.49	Jakobsberg, Sweden	Ramdohr (1956)
Jacobsite	33%	8.505	Weabonga, New South Wales	McAndrew (1952)
Jacobsite	19 to 54%	8.44 to 8.51	various	Mason (1947)
Jacobsite	54%	8.51	Negev, Israel	Katz (1959)
Manganese ferrite ($MnFe_2O_4$)	33%	8.515	synthetic	Economos (1955)
Manganese ferrite ($MnFe_2O_4$)	33%	8.507	synthetic	Gorter (1954)
Manganese ferrite ($MnFe_2O_4$)	33%	8.517	synthetic	Hastings & Corliss (1954)

ment. Hastings and Corliss (1954) made a neutron diffraction study of the distribution of the Mn^{+2} and Mn^{+3} cations amongst the A and B sublattice sites. They found no appreciable change in lattice constant or in Mn^{+2} and Mn^{+3} distribution in samples prepared either in air or nitrogen and subsequently either slow cooled or quenched. It is apparent that the lattice constant of synthetic manganese ferrite does not agree with the findings of Mason and Van Hook & Keith of about 8.46 Å for the .33 mol per cent Mn_3O_4 composition. Mason *et al.*, however, only knew the Fe/Mn ratio of their samples and had no idea of the valence states and distribution of the manganese cations. Hence direct comparison of the two sets of data is not possible. In work with mineralogical specimens, the effect of impurity cations must be further considered. For these reasons the composition of the Negev specimen has been tentatively determined on the basis of Mason's *et al.* work as 54 mol per cent Mn_3O_4 and 46 mol per cent Fe_3O_4.

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FULLER'S EARTH AS AN AGENT FOR PURIFYING HEAVY ORGANIC LIQUIDS*

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For several years we have been investigating trace amounts of metals in various rocks and minerals. Bromoform, diiodomethane (methylene iodide), and acetylene tetrabromide were used to separate igneous rocks into their constituent minerals. Because, in some cases, we were determining low level metal content (1 or 2 ppm.) in mineral separates it became important to know if the liquids could pick up enough metal to contaminate the minerals, and, if so, how the metal might be removed. The concern deepened when our colleage A. P. Pierce told us that bromoform picked up important amounts of uranium, and J. C. Antweiler noted that

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