

distortion to ionic solids are thus explained. The failure of wave-mechanical treatments of isolated  $ML_6$  systems to provide a satisfactory explanation of the  $c/a < 1$  configuration in crystals is also understandable.

The possibility of polymorphism clearly arises in many structures containing tetragonally distorted octahedra: in general the structure with  $c/a < 1$  has lower volume and entropy, and will be the low temperature high pressure form.

*Acknowledgements.* I should like to thank Dr. R. G. Burns, Dr. J. D. C. McConnell, and Dr. L. E. Orgel for reading and commenting on parts of the manuscript. Any remaining errors are mine alone. Financial support has been received from the Science Research Council.

*Department of Mineralogy and Petrology,  
Downing Place,  
Cambridge.*

R. G. J. STRENS

#### *References*

- BILLY (C.) and HAENDLER (H. M.), 1957. Journ. Amer. Chem. Soc., vol. 79, p. 1049.  
BURNHAM (C. W.) and BUERGER (M. J.), 1961. Zeits. Krist., vol. 115, p. 269.  
EDWARDS (A. J.) and PEACOCK (R. D.), 1959. Journ. Chem. Soc., p. 4126.  
ITO (T.), MORIMOTO (N.), and SADANAGA (R.), 1954. Acta Cryst., vol. 7, p. 53.  
JACK (K. H.) and MATTLAND (R.), 1957. Proc. Chem. Soc., p. 232.  
KNOX (K.), 1959. Journ. Chem. Phys., vol. 30, p. 991.  
LIEHR (A. D.) and BALLHAUSEN (C. J.), 1958. Ann. Physics, vol. 3, p. 304.  
OPIK (U.) and PRYCE (M. H. L.), 1957. Proc. Roy. Soc. A, vol. 238, p. 425.  
ORGEL (L. E.), 1960. An introduction to transition metal chemistry, Methuen, London.  
PRYCE (M. H. L.), SINHA (K. P.), and TANABE (Y.), 1965. Mol. Phys., vol. 9, p. 33.

[Manuscript received 19 September 1965]

---

### *Authigenic ferriferous aragonite from bottom sediments of the Adriatic sea*

PETROGRAPHIC analysis of sandy fractions of bottom sediments recently cored in the Gulf of Venice shows a high percentage of coarse carbonate constituents, consisting partly of rounded, detrital grains of limestone and dolomite (brought into the sea by Venetian rivers) and partly of irregular fragments, flat crusts, and occasionally rounded concretions of non-skeletal, micro-crystalline carbonates. These latter are usually yellowish to brownish in colour on account of the contaminating ferruginous material (Damiani, Favretto, Lenardon, and Morelli, 1964).

In thin section these micro-crystalline carbonates show a texture that, for the most part, appears in more or less regular superposition of carbonate layers with intermixed microgranular pyrite occasionally changed into iron oxides. Sometimes each layer consists of carbonate needles that display a random tangential orientation to the surface of the layer itself, but more frequently it simply consists of an aggregation of microgranular carbonate minerals. These needles, or grains, are too small to permit their mineralogical characterization under the polarizing microscope.

The special pattern of these concretions, taken in conjunction with the inclusion of pyrite, confirms unequivocally its authigenic origin.

From a heavy liquid separation (bromoform,  $D = 2.86$ ) two fractions are obtained that, in a preliminary X-ray diffraction analysis, show a different mineralogical composition notwithstanding their apparent morphological similarity. In fact, while the  $< 2.86$  fraction contains essentially a trigonal, calcite-like phase rich in iron (up to 15% by weight, expressed as  $\text{FeCO}_3$ ), the  $> 2.86$  fraction is mainly represented by an orthorhombic, aragonite-like one.

Several aragonite grains were selected from the  $> 2.86$  material under the microscope, the purity of these grains being afterwards checked by X-ray methods. Chemical analysis carried out on solution of these grains in cold 0.1 *N* hydrochloric acid and expressed in terms of carbonates, gave:  $\text{CaCO}_3$  93.6,  $\text{FeCO}_3$  4.1, insoluble residuum 2.8; sum 100.5. The residue, under X-ray examination, revealed the presence of pyrite and goethite. From this it appears that the aragonite, like the calcite, shows a low but not negligible iron content, though traces of contaminating iron oxides may have gone into solution under the mild acid attack.

In order to confirm the possibility of  $\text{Fe}^{2+}$  accommodation in the lattice of aragonite, a detailed X-ray examination was made using a standard of 114.6 mm diameter powder camera (Straumanis mounting) and  $\text{Fe-K}\alpha$  (Mn filtered) radiation. After indexing by comparison with the standard aragonite pattern (Swanson, Fuyat, and Ugrinič, 1954), the unit-cell constants were computed from the interplanar spacings corresponding to the sharpest non-multiple diffraction maxima. A least-squares method was employed (Cramer, 1954) giving the same weight to every reflection considered. The unit cell parameters are:  $a$   $4.933 \pm 0.004$  Å,  $b$   $7.950 \pm 0.006$  Å,  $c$   $5.731 \pm 0.005$  Å. Cell volume  $224.7$  Å<sup>3</sup>. In comparison to that of standard aragonite (*loc. cit.*) for which  $a$  4.959 Å,  $b$  7.968 Å,  $c$  5.741 Å (confidence limits not specified),

cell volume  $226.8 \text{ \AA}^3$ , the unit cell is slightly contracted, indicating, therefore, a certain degree of  $\text{Fe}^{2+}$  substitution.

Sedimentary ferrous aragonite seems to be rare, as is Mg-containing aragonite. In the literature, the maximum Mg content reported for aragonite, taken from shells of calcareous marine organisms, is about 1%  $\text{MgCO}_3$  by weight (Chave, 1954). Considering that the ionic radius of  $\text{Mg}^{2+}$  ( $0.66 \text{ \AA}$ ) is smaller than that of  $\text{Fe}^{2+}$  ( $0.74 \text{ \AA}$ ), a greater substitution for the latter seems to be acceptable and the value of about 4%  $\text{FeCO}_3$  might be near to the maximum permitted. As a result of cation substitution, the lattice shows a certain degree of disorder, as may be deduced from the broadening of the diffraction lines in the back-reflection region of the X-ray photograph.

As regards the origin of these ferrous aragonitic concretions, microscopic observations suggest a chemical deposition while the neogenesis of the associated pyrite indicates an environment where both the reducing potential and mobility of iron are high. Similar conditions appear to favour the precipitation of ferruginous carbonate, as has been pointed out by Komachev (1963) who found chemical precipitates of iron-containing calcium carbonate in the sediments of the Caspian Sea.

*Acknowledgements.* The author is very indebted to Prof. S. Morgante, Director of the Istituto di Mineralogia at Trieste University, for assistance in numerous ways; to Dr. G. Lenardon, who kindly supplied the samples; and to Prof. L. Trotti, Director of the Istituto Sperimentale Talassografico of Trieste, for encouragement and various facilities in the final stages of the work.

*Istituto Sperimentale Talassografico*  
*Istituto di Mineralogia dell'Università*  
*Trieste, Italy*

L. FAVRETTO

Present address: Department of Chemistry, University of Trieste.

#### References

- CHAVE (K. E.), 1954. *Journ. Geol.*, vol. 62, p. 266.  
CRAMER (H.), 1954. *The Elements of Probability Theory*, p. 235. Almqvist & Wiksell, Stockholm.  
DAMIANI (A.), FAVRETTO (L.), LENARDON (G.), and MORELLI (G. L.), 1964. *Inst. Mineralogy Publ.* no. 14, Trieste University.  
KOMACHEV (V. G.) [КОМАЧЕВ (В. Г.)] 1963. *Dokl. Acad. Sci., Earth Sci. Sect.* (Engl. transl. of Докл. Акад. Наук СССР), vol. 139, p. 677.  
SWANSON (H. E.), FUYAT (R. K.), and UGRINIĆ (G. M.), 1954. *Nat. Bur. Stand. Circular* no. 539, vol. III, p. 53.

[*Manuscript received 12 September 1965*]