

12. On large fluid inclosures in gypsum from Sicily ¹

by

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In the autumn of 1892 I acquired through mr E. FOOTE, dealer in minerals at Philadelphia, a serie of very fine crystals of sulphur from Cianciana, the old well-known locality of minerals in the district of Girgenti, island of Sicily, and, together with them, excellent representatives of the associated minerals, aragonite and gypsum. Some specimens of the latter mineral are particularly interesting on account of the liquid inclusions which they contain.

The gypsum is developed in extraordinarily large crystal individuals, a couple of them measuring 0,3 m. in length. The crystals have originally been lenticular in form; when I obtained them, they were divided in two along the most distinct cleavage b (010), and consequently present a semilenticular shape. The crystals are colourless and clear and, notwithstanding their considerable dimensions, perfectly transparent.

Some of the liquid inclosures are large, irregular in form, and branched, measuring 20 to 30 mm. in extent, others are rather thin, flat, and extending along the plane of the most distinct cleavage. In all of them a libella is observable, which does not perceptibly diminish in size when the crystal is slightly heated.

As the enclosed fluid may be assumed to be the mother-liquor from which the gypsum as well as the sulphur have crystallized, I thought that a chemical examination would be of some interest.

With this view a boring was made to one of the largest inclosures, and the fluid was extracted by means of a small pipe made for the purpose. About 3 cub.cm. of fluid were obtained. On boring, sulphuretted hydrogen escaped, but the pressure of the gas does not seem to have been very great, for when the inclosure was reached by the bore, the gas escaped quietly and noiselessly, and no formation of gas-bubbles in the liquid was observed.

¹ The chief substance of this paper has been previously published in Geol. Fören:s i Stockholm Förhandl. Vol. 15, p. 136, 1893.

The gas was not examined. It is, however, probable, that it consists, chiefly or exclusively, of H_2S . The same gas seems to be enclosed in small pores in the gypsum, to judge from the fact that a strong smell of H_2S is emitted on the crystals being divided along the most distinct cleavage. The solution, which gave a neutral — at least not an acid — reaction, has been analyzed by mr R. MAUZELIUS.

The liquid obtained was weighed and then allowed to stand a few hours, during which time a small quantity of sulphur was separated out as a thin film on the surface of the fluid. The fluid was then filtered, whereupon the solution was evaporated in a water-bath, and the residue was dried at a temperature of $+115^\circ$ C. After having been weighed the salts were dissolved in 3 to 4 cub.cm. of water. The solution, which was somewhat turbid, became clear on the addition of a drop of nitric acid, on which a few diminutive gas-bubbles escaped, indicating the presence of an indeterminable quantity of carbon dioxide. The solution was then diluted, and the constituents were determined by the usual methods.

The saline constituents were 4,023 p. c. of the solution.

The analysis gave the following result:

K_2O	2.1 %
Na_2O	40.9
CaO	4.1
MgO	3.9
Cl	44.9
SO_3	14.1
	110.0
Deduct O for Cl_2	10.1
	99.9

The analysis shows an excess of basic constituents, which might be thought to be due to some negative ingredient — *e. g.* carbonic acid or sulphur — having been overlooked. However, this is made very improbable not only by the circumstance that, on the salts being dissolved in a solution containing nitric acid, no noteworthy generation of gas took place — which excludes the presence of a determinable quantity of CO_2 — but also, and above all, by the fact that the analysis shows no loss. Taking into consideration the circumstance that the analysis was made on the residue, dried at $+115^\circ$ C., a more probable explanation offers. On being dried, chloride of magnesium loses part of its chlorine, basic salts of varying composition being formed. Supposing this to have taken place in the present case, and consequently the seeming excess of bases to depend on a loss of chlorine during the drying process of the salt-mass, the solution has contained, besides H_2S ,

K	0.068 p. c.
Na.	1.198
Ca.	0.114
Mg	0.092
Cl.	1.883
SO ₄	0.668
amount of salts	4.023,

or in percentage of the salts contained in the solution

K ₂ SO ₄	3.7 %
Na ₂ SO ₄	11.4
CaSO ₄	9.7
NaCl.	66.2
MgCl ₂	9.0
	100.0.

A comparison will immediately show how near this water is to the water of the ocean with regard to the chemical composition. Comparing, first, the percentage amount of salts, we find great accordance, the average percentage of salts in the ocean water being 3.43¹, in the water of the inclusion 4.02 p. c.; the latter consequently contains very little more salts. On further comparison with reference to the ingredients we find that NaCl is the chief component of both, and that the rest of the ingredients are the same, though entering in different proportions. The principal difference is that the inclosure contains a greater proportion of sulphates, as appears from the subjoined table:

	Sulphates	Chlorides
In oceanic water	10.34 %	89.45 %
In the inclosure	24.8 »	75.2 »

In short, the fluid in the cavity of the gypsum may be said to be of the same type as the water of the ocean, only differing from it by containing a greater percentage of sulphates.

Another point worth noticing is the very great agreement of this water with that of several sulphurous springs. Of these we choose for a comparison the noted Kaiserquelle at Aix-la-Chapelle. The percentage of salts in this spring is 4.0794, consequently very nearly the same as in the analyzed water from the inclusion.

¹ Here and in the following pages of this paper in speaking of the composition of oceanic water I give the figures of FORCHHAMMER, as quoted by ROTH, Allgem. u. Chem. Geol. Vol. I. p. 493.

The following table shows the points of difference and agreement between oceanic water, the water of the Kaiserquelle and that of the inclosure.

	NaCl	KCl	MgCl ₂	MgSO ₄	CaSO ₄	Na ₂ SO ₄	K ₂ SO ₄	CaCO ₃	MgCO ₃	Na ₂ CO ₃	Other salts	Total of salts
Oceanic water	78.32	1.69	9.44	6.40	3.94	—	—	—	—	—	0.21	3.440
Kaiserquelle	64.13	—	—	—	—	6.95	3.74	3.87	1.24	15.81	4.25 ¹	4.079
The inclosure	66.2	—	9.0	—	9.7	11.4	3.7	—	—	—	—	4.023

The difference depends on the percentage of carbonates in the spring-water, which are almost totally absent from the water enclosed in the gypsum.

The water analyzed is consequently very near in composition to the water of the ocean as well as to that of certain springs of the present time, and it cannot be decided with certainty to which of these kinds of water it is to be referred with regard to its origin.

On the whole, the fluid enclosed in the gypsum may be regarded as a *fossile water from the miocæn age*.

The Sicilian deposits of sulphur generally occur in clays and marls belonging to the sarmatic series². They have consequently formed in an inland sea; and inclusions of a fluid so nearly agreeing with sea-water cannot, therefore, be surprising.

However, the chemical character of the fluid seems to be suited to illustrate the much debated question as to the formation of sulphur, gypsum etc. in Sicily.

As is known, two different views have been advanced, to explain the formation of these sulphur deposits. According to one of these views the sulphur owes its origin to a reduction of gypsum through the agency of organic matters, which reduction is presumed to have taken place in deposits from lagoons and bays cut off from the main body of the sea, where the less soluble salts contained in the sea-water have been precipitated³. It might then be expected that the solution should present the same characters as the mother-liquor after the concentration of the sea-water, but if we compare the composition of the enclosed fluid, the analysis of which has been given above, with such a mother-liquor, we find

¹ Consisting of Na₂S, FeCO₃, SrCO₃, Li₂CO₃, NaBr, NaJ, SiO₂, and organic substances. J. ROTH, Allgem. u. Chem. Geologie, Vol. I, p. 446.

² Whether this is the case with the occurrences of sulphur at Cianciana, I do not know, but I have no reason for supposing them to differ in this respect from other occurrences of sulphur in Sicily.

³ A. GEIKIE, Textbook of Geology, 1st Ed. 1882, p. 332. — FUCHS et DELAUNAY, Traité des gîtes minéraux, 1893. Tome I, p. 274.

differences of great importance. In real mother-liquors (the Elton lake, the Karabugas bay for instance) one finds a comparatively low percentage of NaCl, this constituent having already been deposited, and high percentages of the easily soluble salts Mg Cl and Mg SO₄, and, besides, gypsum is totally absent from such a water. In all these respects the liquid analysed differs from a mother-liquor of sea-water.

According to the other view the sulphur is a deposit from springs containing H₂S or sulphides of alkalis and alkaline earths ¹.

It may then be presumed that the springwaters have had the very same composition as the enclosed fluid, and that the sulphur as well as the gypsum have been deposited directly from these springwaters. This view seems to be identical with the one lately advanced by G. SPEZZIA ², and its correctness is confirmed by the nature of the water here analyzed, which very nearly agrees with that of several existing spring-waters. Or it may be supposed that in a lagoon or a bay cut off from the sea at different periods, emanations of H₂S have taken place; the sulphuretted hydrogen has, in decomposing given rise to deposits of native sulphur and to sulphuric acid, which has attacked the limestone and marls in the surroundings, thus adding to the amount of sulphates, chiefly of gypsum, contained in the water. On crystallizing, the gypsum has enclosed in cavities a quantity of the solution as well as of the rising H₂S gas.

Which of these explanations is the true one, can be decided only by investigations made at the place.

¹ J. ROTH, Allgem. und Chem. Geologie, Vol. I, p. 448.

² Sull' origine del solfo nei giacimenti soliferi della Sicilia. Torino 1892.

