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GLACIAL INFLUENCE ON NEOGENE EVAPORITES

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Abstract

Sulfatization of Sicilian potash beds is taken to be due to inflow of meteoric waters charged with dissolved calcium sulfate eroded from exposed marginal shelf areas by rain during a glacial lowering of sea level.

Introduction

Evaporite research has deep roots in the Mediterranean region. J. Usiglio published his chart of sequential precipitation from Mediterranean seawater in 1849. It contained a sequence different from that observed in salt mines, as epsom salts were precipitated nearly concurrently with halite because the seawater evaporation experiment took place in a well oxygenated laboratory. Most evaporite basins produce early anoxic conditions during progressive brine concentration; a bloom of anaerobic sulfur bacteria strips sulfate ions of their oxygen. A sulfate deficiency develops despite the influx of three times as many sulfate ions as consumed by precipitating gypsum (Borchert, 1969); only calcium sulfate and no other sulfate is deposited.

Sicilian potash deposits are sulfatized just as all Neogene and Permian deposits. This potash sulfatization is secondary. Sulfatizing waters did not enter potash horizons at any other time during the Phanerozoic (Sonnenfeld, 1985a). Special circumstances must have prevailed in these two time intervals to allow potash sulfatization to proceed.

An earlier idea that the dewatering of basal gypsum supplied the required sulfate ions (Borchert and Muir, 1964) is no longer tenable, as basal anhydrite thicknesses are more than one order of magnitude too small to account for the sulfate required (Sonnenfeld, 1984). Warm halite-saturated brines are hygroscopic enough to dewater porous gypsum beds. Resulting anhydrite beds are then not deformed due to volume reduction, as would happen in a conversion after compaction of the overlying halite.

Because magnesium chloride is less soluble in a sulfatic brine than in a chloridic one, the mineral bischofite (the hydrated magnesium chloride) has primarily been found in sulfatized potash deposits, while replacement of magnesium or potassium by iron is rare in sulfatized horizons on account of an increased solubility of iron sulfates.

Source of sulfatic brines

Oxygenated, sulfatic brines can only form at or near the earth surface; connate formation waters are invariably anoxic. Sulfatization thus requires two conditions: an influx of meteoric waters from a surface source and a mode of entering into a salt sequence normally impervious to aqueous solutions.

A source of surface brines is not difficult to find: Sonnenfeld (1984) proposed a model of evaporite basins with continuous water exchange through the entrance strait and broad saturation shelves precipitating gypsum and covering triple the area of the region of rapid synsedimentary subsidence, and massive halite precipitation following upon an initial modest gypsum deposition. This model was first developed on water exchange and depositional history of the modern Mediterranean Sea and presented in simplified form at the Monaco reunion (Sonnenfeld, 1975). While basal gypsum is insufficient to supply adequate sulfate ions, the gypsum wall of marginal saturation shelves would be more than adequate, if they became exposed to meteoric erosion. The solute could then seep into porous beds. Indeed, in Sicily the isotopic signature of both Messinian calcium carbonates and sulfates has been altered by a post-depositional influx of meteoric waters (Longinelli and Ricchiuto, 1977; Longinelli et al., 1978; Longinelli, 1979; Censi et al., 1980; Kushnir, 1982). These seepages were thus either Pliocene or Pleistocene in age.

It is here suggested that such exposure occurred primarily during sea level lowering in glacial stages when vast quantities of water were trapped in continental glaciation. During both the Quaternary and the Permian, major ice caps formed in polar regions, lowering the world sea level. The shore moved seaward and exposed subaerially the continental shelves where gypsum had been precipitated. Winter rains then dissolved some of the calcium sulfate and the runoff drained the solute: it could easily enter as yet uncompacted evaporites. Gypsum and limestone beds are frequently bent basinward along the shelf margin, dipping at a progressively steeper angle into the area of more rapid synsedimentary subsidence, the area of chloride precipitation. There is thus a regional gradient towards shelf slopes.

Flash floods drop their bedload of sand grains onto the gypsum shelf and carry clay particles far into the basin. The settling out clay particles form clay laminae, which remain permeable for a long time after salt precipitation has recommenced (Sonnenfeld and Hudec, 1985). Although rock salt is virtually impermeable to aqueous solutions, clay layers remain open to circulating brines until they are buried deeply and compaction expels the entrapped waters laterally.

Sulfatizing solutions did not have to travel far to reach potash beds, as potash precipitation occurred preferentially on the slopes of the rapidly subsiding part of the basin and frequently thickened shoreward (Sonnenfeld, 1984). The potash mine at Caltanissetta in Sicily is likewise located in a marginal bay not too far from the ancient bay shelf.

Tenor of the potash ores

There are only two common primary potash minerals, sylvite and carnallite. In contrast, there is a great variety of K-Mg-sulfate minerals, most of which are hydrated. Partially sulfatized kainite can decompose to a secondary sylvite. Complete sulfatization leads to K-Mg-sulfate minerals; their hydration decreasing with rising temperature and thus increasing burial before conversion. All of these minerals yield a higher percentage of potassium oxide than even pure carnallite (Sonnenfeld, 1985b); sulfatization thus enhances the tenor of potash ores. Excess magnesium is precipitated either as sulfate or as chloride.

Polyhalite, the K-Mg-alteration of gypsum, is found along salt basin margins or as alteration of gypsum stringers in the halite sequence. Na-, Na-K-, or Na-Mg-sulfate minerals form wherever there was a substantial influx of meteoric waters, occur in lenses and nests rather than in beds, and are of no commercial value.

Conclusion

Glacial sea level lowering is responsible for the exposure and dissolution of gypsum deposits on the marginal shelves. The runoff travels downdip into the basin and can penetrate along a clay layer into the salt sequence and react with potassium chlorides. Sicilian potash beds are sulfatized. This sulfatization is considered to be due to inflow of meteoric waters charged with dissolved calcium sulfate eroded from exposed marginal shelf areas.

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G-III1

DEEP STRUCTURE AND DYNAMICS ALONG THE SOUTHERN SEGMENT OF THE EUROPEAN GEOTRAVERSE

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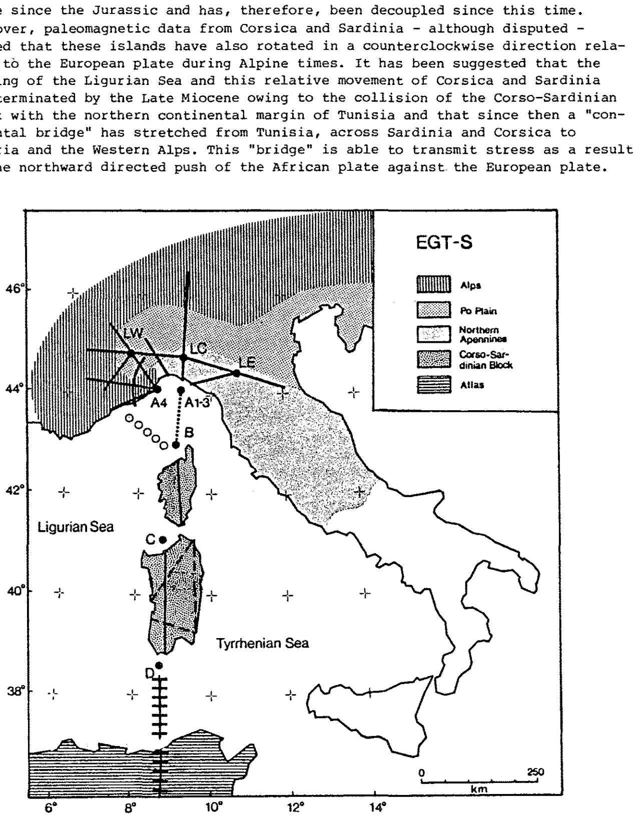
The "European Geotraverse" is an international multidisciplinary project involving the collaborative efforts of many earth scientists from several European countries. It is focussed on a north-south oriented lithospheric profile, about 4000 km long and of varying width, extending from northernmost Scandinavia to North Africa. This profile consists of three interlinking segments (Northern, Central and Southern) comprising a continuous succession of tectonic provinces ranging from the oldest Precambrian areas of the Baltic shield to the currently active area of the Western Mediterranean. The broad aim of the "European Geotraverse" is to obtain a three-dimensional picture of the structure, state and composition of the lithosphere as a basis for an understanding of its evolution and dynamics.

Since 1982 the Southern Segment of the "European Geotraverse" has been the target of intensive geological and geophysical studies. This Segment encompasses the Central, Southern and Western Alps, the Po Basin, the Northern Apeninnes, the Ligurian and Tyrrhenian Seas, Corsica and Sardinia, the Sardinian and Sicilian Channels, and the complex geological structures of Tunisia. Exceptionally good data from a series of seismic experiments carried out in 1982, 1983 and 1985 have led to a detailed picture of lithospheric structure along the Southern Segment.

The crust attains its maximum thickness of 55 to 60 km beneath the southernmost part of the Central Alps. Two "crust-mantle"-like interfaces (at 35 and 50 km depth) seem to exist beneath the Po Basin, while from the Northern Apeninnes to the Ligurian coast the crustal thickness decreases from about 40 km to 20-25 km. A detailed three-dimensional analysis of newly collected gravimetric data along a profile from the northern foreland of the Alps southward to the Gulf of Genoa corroborate the hypothesis, based previously on seismological and geological data, that a 200 km wide zone of relatively dense and cold subducted lithosphere, centered beneath the Southern Alps and the northern part of the Po Basin, extends to depths of 150 to 200 km.

In the area between Genoa and Corsica the Ligurian Sea is underlain by a greatly thinned, distinctively layered section of continental crust and an upper mantle with an anomalously low P_n-velocity of only 7.5 km/s. The data for both crustal and upper mantle structure are suggestive of incipient rifting. In addition it became clear that the island chain of Corsica and Sardinia is underlain by bowl-shaped "typically" Hercynian continental crusts with a total lithospheric thickness of 60 to 70 km.

Paleomagnetic data obtained for the Southern Alps, Istria, Umbria, Gargano and Sicily indicate that the Adriatic microplate, although having African affinities, has rotated between 15^0 and 30^0 counterclockwise relative to the African plate since the Jurassic and has, therefore, been decoupled since this time. Moreover, paleomagnetic data from Corsica and Sardinia - although disputed - showed that these islands have also rotated in a counterclockwise direction relative to the European plate during Alpine times. It has been suggested that the opening of the Ligurian Sea and this relative movement of Corsica and Sardinia had terminated by the Late Miocene owing to the collision of the Corso-Sardinian block with the northern continental margin of Tunisia and that since then a "continental bridge" has stretched from Tunisia, across Sardinia and Corsica to Liguria and the Western Alps. This "bridge" is able to transmit stress as a result of the northward directed push of the African plate against the European plate.



The black lines indicate seismic refraction profiles (1982-1985).