PARENTAL BRINE EVOLUTION IN THE CHILEAN NITRATE DEPOSITS (Pedro de Valdivia, II Región de Antofagasta). MINERALOGICAL AND PETROGRAPHIC DATA

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INTRODUCTION

The Chilean nitrate deposits have been formed by complex paragenesis of saline minerals (locally named *caliche*) that infill the porosity of rocks ranging in age from Paleozoic to Cenozoic. Minerals which are normally extremely rare - nitrates, nitrate-sulphates, iodates and iodate-sulphates - are common in the Chilean nitrates. Located in the Atacama Desert (North Chile; between 19°30' and 25°30' S latitude, and 69°30' and 70°30' W longitude), the deposits follow an irregular N-S swathe, a few km wide (reaching a maximum of several tens of km). The distribution of the deposits parallels the contact between the Coastal Range and the Central Depression.

The nitrate (and saline) ores can infill either cracks (joints, fractures) in the country rocks (volcanic, intrusive or sedimentary), porosity in breccias and conglomerates from alluvial fans and pediments, or porosity created by previous alteration processes. Ericksen (1981) divided the different styles of occurrence as *deposits in rock* and *sedimentary deposits.* Deposits in rock are characterized by

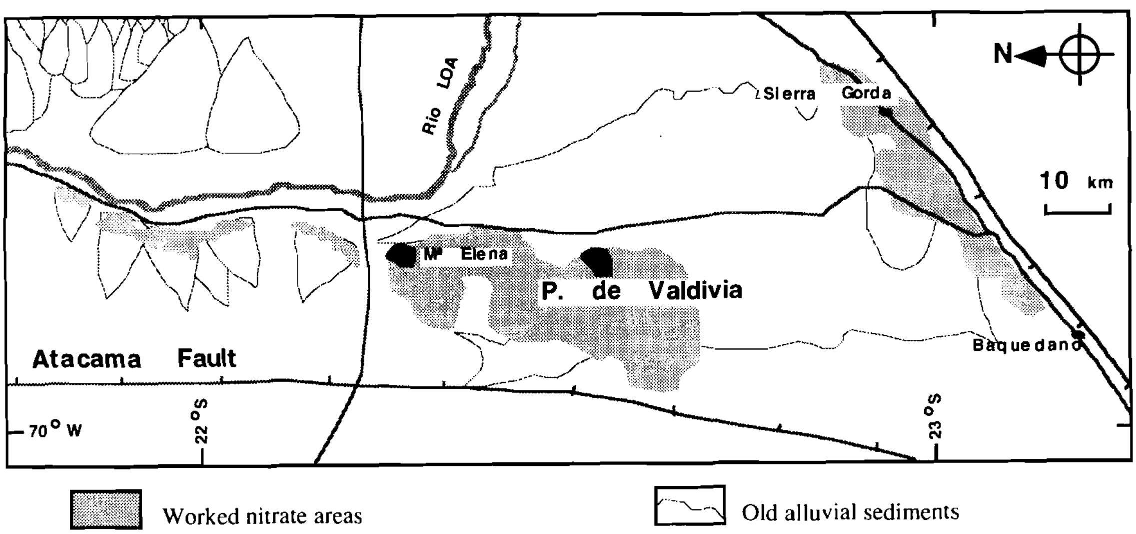

Fig. 1. Distribution of worked nitrate areas in the Pedro de Valdivia area. See the relationships between the nitrate deposits and tertiary alluvial sediments on the NW alluvial fans.

open fracture systems, and so can reach high local concentrations in sodium chloride and nitrate. Sedimentary deposits are characterized by narrow pore spaces, commonly millimetre-scale or smaller.

The Pedro de Valdivia deposit is located 160 km to the NNE of Antofagasta (22°45' S, 69°40' W), close to the centre of the area in which nitrate occur, in the Chilean Central Depression. It extends over a width of about 15km, and is elongated 40km in the N-S direction (Fig. 1). The altitude is 1500m on average, the topography being very uniform (±200m). The geological setting (Araya & Toro, 1983) is dominated by volcanic and intrusive rocks. The volcanic sequence is Jurassic (350m of andesitic flows -*La Negra Formation*), Cretaceous? (150m of acid piroclastic tuffs and breccias), Paleocene-Eocene (150m of tuffs and ignimbrites), Miocene (alluvial clastic and volcanoclastic rocks -bearing the nitrate-ore; Fig.1-) and finally (overlying in angular discordance the previous materials) Quaternary unconsolidated alluvium and colluvium. Intrusives are represented by mesozoic granites and monzodiorites, and cenozoic acid porphyries. The fault system has a dominant N-S trend, with subordinate trends to about N40E and E-W. Nitrate ores occur within the Miocene sediments (*caliche negro*) and are also present as disseminations (and infilling voids) in the sustrate rocks (*caliche blanco*) (Chong, 1991, 1994). The ore (running at less than 11% NO_3) can reach depths of 10m, more commonly being less than 3m deep.

PETROGRAPHY AND PARAGENETIC RELATIONSHIPS

SEM, optical mineralogy and XRD have been used to identify the minerals (Table 1) in the Pedro de Valdivia deposit.

Table 1

Chlorides:	Halite	$NaCl$
Sulphates:	Anhydrite	$CaSO_4$
	Bloedite	$Na_2Mg(SO_4)_2.4H_2O$
	Glauberite	$Na_2Ca(SO_4)_2$
	Gypsum	$CaSO_4.2H_2O$
	Löweite	$Na_{12}Mg_7(SO_4)_{13}.15H_2O$
	Polyhalite	$Ca_2MgK_2(SO_4)_4.2H_2O$
	Starkeyite	$MgSO_4.4H_2O$
	Thenardite	Na_2SO_4
Carbonates:	Calcite	$CaCO_3$
Nitrates:	Nitratine	$NaNO_3$
	Niter	KNO_3
	Darapskite	$Na_3[NO_3SO_4].H_2O$
	Humberstonite	$K_3Na_7Mg_2[(NO_3)_2(SO_4)_6].6H_2O$
Borates:	Kaliborite	$KMg_2H[B_6O_8(OH)_5]_2.4H_2O$
	Probertite	$NaCa[(B_5O_7)(OH)_4].3H_2O$
Iodates:	Lautarite	$Ca(IO_3)_2$
	Hectorfloresite	$Na_9[(IO_3)(SO_4)_4]$
	Fuenzalidaite	$K_6(Na,K)_4Na_6Mg_{10}(SO_4)_{12}(IO_3)_{12}.12H_2O$
Chromates:	Dietzeite	$Ca_2[(IO_3)_2CrO_4]$
Oxides:	Hematites	Fe_2O_3
Silicates:	Quartz, heulandite, laumontite.	

The petrographic study shows that interstitial processes (Chong & Pueyo, 1992) are the main control on mineralisation in both kind of deposits (*sedimentary* and *in rock*). In the Pedro de Valdivia area these processes are principally controled by the composition of the volcanic host rock and the strongly saline solutions from which the ore minerals precipitate.

The precipitation sequence and arrangement of minerals is as follows:

a) Submillimetre-scale fissures in a silicate host mineral showing a first generation of halite in the walls and a central infilling of nitratine or, sometimes, mixtures of saline minerals (halite, nitratine, darapskite). Ocassionally, the first salt generation is euhedral to subhedral.

b) Residual porosity in the saline precipitate itself, forming geodes, where halite and nitratine coprecipitate. Geode cavities develop in a mass formed by the silicate matrix and saline minerals (halite, nitratine, humberstonite, darapskite). Halite and nitratine represent the last interstitial precipitates. Euhedral iodates (lautarite, hectorfloresite, and fuenzalidaite) and borates (probertite) coprecipitate in the residual porosity.

c) Subcentimetre-scale fissures in the host rock, infilled by a first generation of zeolite (commonly heulandite or laumontite), followed by another generation of coarse sparry calcite. This sequence can be recurrent, each couplet being separated by dissolution surfaces. Both minerals, zeolite and calcite, are present as mm-size cristals. A final zeolite generation is followed by sulphate mineral precipitation (anhydrite, glauberite). Moreover, the rock shows fissures between, around, and inside the grains, following exfoliation planes. These fissures, μm in size, are total or partially infilled by anhydrite, glauberite, halite or nitratine.

d) Porosity almost totally obliterated by saline materials, where the last generation is nitratine. Nitratine infills previous voids between halite, glauberite, and silicate matrix. Nitratine exhibits abundant inclusions and triple junction voids. A sequence of minerals (nitratine between halite grains, and niter, lautarite, dietzeite, hectorfloresite and fuenzalidaite within nitratine) which precipitate in these voids represent the last stages of evolution of the residual brine.

e) Submillimetre-scale fissures in the host rock, infilled by the sequence polyhalite (fibrous radiated), anhydrite, and nitratine. Other irregular porosities are infilled by euhedral, μm-size bloedite (or löweite) and, finally, nitratine.

Other frequently associated minerals are darapskite-nitratine (or -humberstonite) and löweite-bloedite. K-Mg minerals (fuenzalidaite-niter-polyhalite-(sylvite?)) frequently form an association with each other, and also with nitratine or nitratine-halite boundaries. Euhedral tabular kaliborite (μm-size) has been observed in cavities between humberstonite grains.

BRINE EVOLUTION INFERENCES

A synthesis of the precipitation sequences, deduced from petrographic observation, is presented in Figure 2.

The general evolution of brines is as follows:

1) A first precipitation of Ca-bearing minerals (Ca-zeolites - calcite - anhydrite).

2) A group of Na-Ca and Na-Mg (-K) minerals (glauberite - bloedite - polyhalite), defining two main evolutionary trends: a) A Na-trend, represented by the series glauberite - darapskite - (halite - nitratine) - hectorfloresite; and b) A Na-Mg-K trend represented by the series bloedite - (polihalite) - humberstonite - (halite - nitratine) - fuenzalidaite.

The final minerals, which precipitate in the residual porosity, are nitrate-sulfates, iodate-sulfates, iodates, chromates and borates. Commonly these minerals precipitate in the last stages of brine evolution, when (or after) halite and nitratine coprecipitate. These minerals include elements that either are not compatible with previously precipitated minerals, or have not previously been consumed.

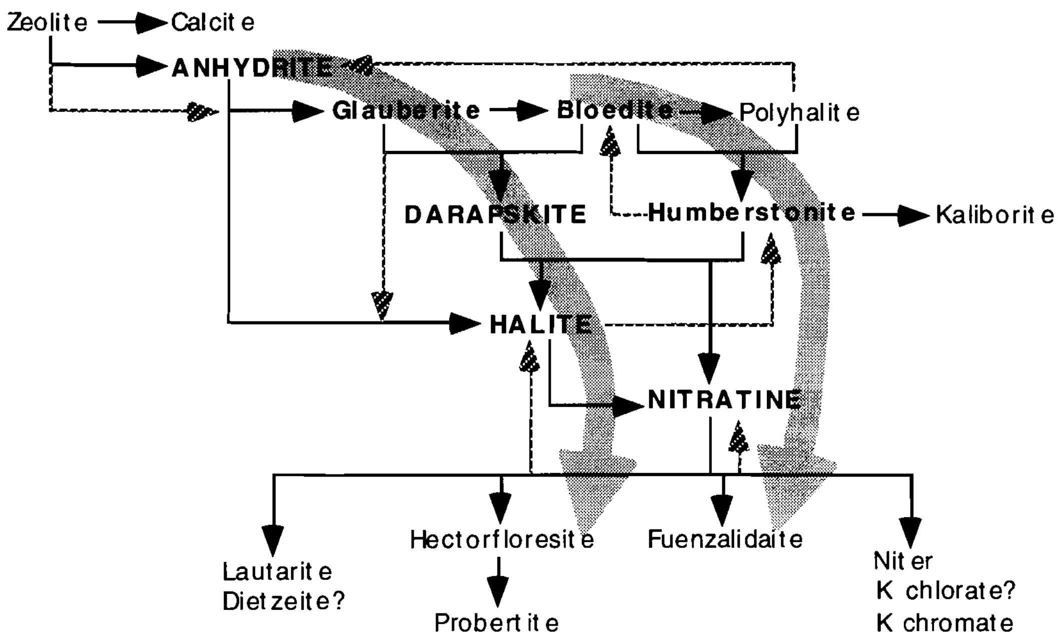

Fig. 2. Synthetic diagram of parental brine evolution in the Pedro de Valdivia deposit. The main paragenetic relationships are indicated in solid lines. The main general trends are marked by thick hatched arrows.

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