

Recent Changes in the Copahue Geothermal Field, Neuquén Province, Argentina

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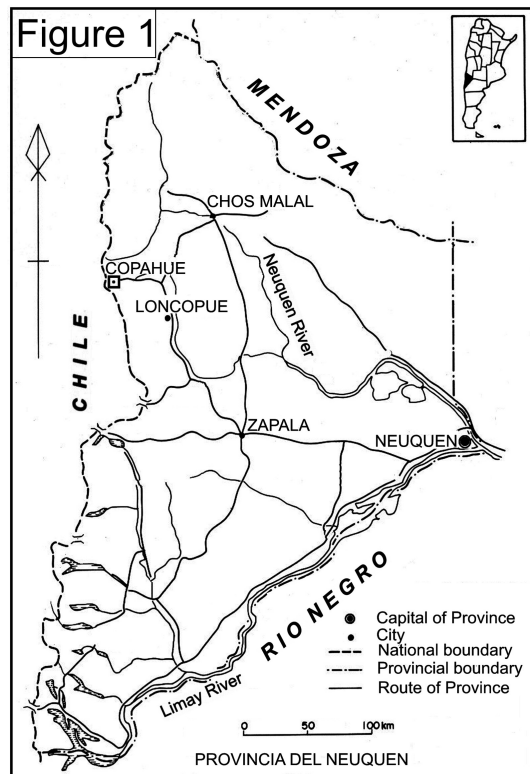
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ABSTRACT

Recent progressive changes that have occurred in the area of Termas de Copahue are described. One of the most conspicuous is the emergence of a new area of geothermal activity on the southern slope of Termas de Copahue, and the other is the presence of minerals of the group of sulphate-carbonate burkeite and hanksite, besides tinkalconite, which is a new mention for this geothermal field.

1. INTRODUCTION

The Copahue volcano is located on the west border of Argentina, in the Neuquén Province, on the Andes Range, nearby the boundary with Chile. (Figure 1) It is about 37° latitude S, 71° longitude W, and the altitude is from 1,600 to 3,000 meters. The studied area is located in a semi elliptical valley of about 15 km NS and 20 km EW.

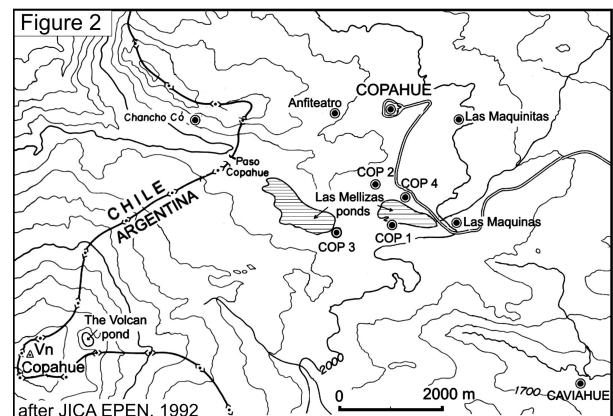


The Copahue Geothermal Field (CGF) is located in a volcanic complex that has suffered a strong influence of tectonic movements from the beginning of its evolution. Regionally, it is possible to recognize two predominant fracture systems, the main system has a N55W direction and the other one is N15W. According to these fracture systems, it is possible to define the strength direction that affected the Neuquén basin since pre-Jurassic times.

The tectonics of the studied area is characterized by a fracture system associated to the evolution of the volcanic complex. Circular faults that constitute the borders of a big caldera were formed in the first stage of the volcanic evolution, developing a radial fault system, observable in the external part of the caldera.

The second stage of the Copahue volcanic complex is represented by a group of several effusive centres: Las Mellizas, Trolon, Bayo and Copahue. Las Mellizas Centre has the largest area. It covers the bottom of the great caldera (15 x 20 km). The effusive centres Trolon, Bayo and Copahue are located on the border of this caldera.

Five main active geothermal manifestations constituted the Copahue Geothermal Field (CGF). There are known as Termas de Copahue, Las Máquinas, Las Máquinitas and El Anfiteatro in Argentine and Chancho Co in Chile. (Figure 2).



The area called Termas de Copahue is one of the largest in the GCC and covers a horseshoe shaped area elongated in WNW-ESE direction. Its original condition is profoundly changed by the construction of the Balneotherapy Centre, hotels and other associated services. This area is the one where the medicinal use of the geothermal resource is more developed and it shows also the presence of dams and pools over or aside the hot springs, which cause the formation of small ponds. The water there is turbid and whitish because the presence of colloidal sulphur and gas that can be seen as bubbles in the surface of water.

The activity of the Copahue Volcano has increased since 1992. The first episode, as mentioned on 1992, was enclosed almost exclusively to the eruption of large amounts of sulphur. On 1995 a second episode of similar characteristics occurred. On 2000 took place the last and largest episode of volcanic activity. In this stage the eruption extended almost six months and consisted mainly of magmatic pyroclastic material, with andesitic composition.

2. RECENT CHANGES IN COPAHUE

2.1. Termas de Copahue

During our regular visits to the CGF in the recent past years it has been observed that some progressive changes in the area of Termas have been taken place. One of the most conspicuous is the emergence of a new area of geothermal activity on the southern slope of Termas de Copahue, where about six years ago there was no significant geothermal activity.

About ten years ago it was merely a bleached area consisting of kaolinite, accompanied by cristobalite, quartz and alunite, interlayered with lenses of a chine texture material formed by poorly crystalline kaolinite and amorphous silica. There were also some glassy crusts and veinlets, consisting mainly of cristobalite and clinoptilolite. The area did not show any fumarolic activity. These characteristics indicate that although the alteration had been caused by geothermal fluids, this activity had ceased at that moment.

Sometime after then, some fumarolic activity surged in the area, and it gradually increased, accompanied by the formation of scabs of efflorescence. The zone is about 20 meters wide and more than 100 meters length, with a N55W direction, coincident with dominant system of the area. (Figures 3 and 4).

Figure 3



Figure 4



This activity was followed by the flowing of hot fluids and the development of large mud pots, collapsed holes and fumaroles. (Figures 5 and 6).



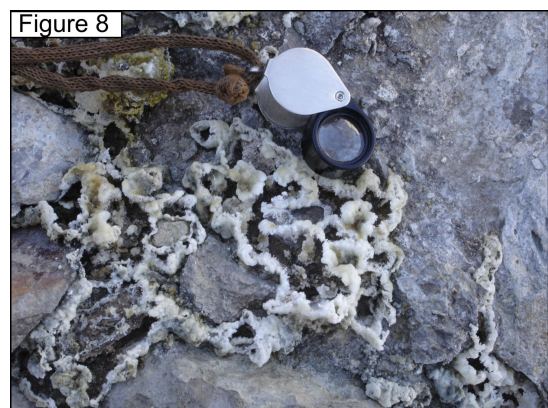
Figure 6



One of the most notable features is the efflorescence formed around the fumaroles and still over the field rocks and filling the small cracks in the ground. These efflorescences generally occur as fibrous sub parallel to radial aggregates of varied colours or as small rounded masses formed by very fine fibers.

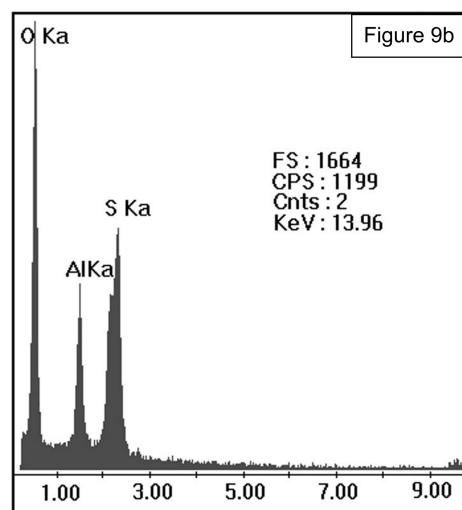
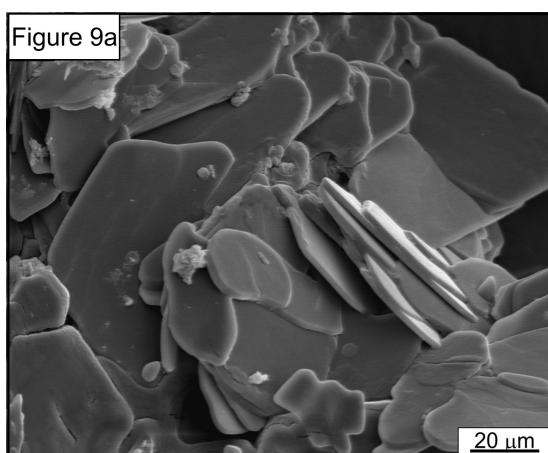
Most of the phases that form this secondary mineral association are very fine-grained, so they were identified by means of X-ray diffraction (XRD). Scanning electron microscopy (SEM) with an energy dispersive X-ray analyzer was used to confirm XRD mineral identification. These analyses allowed to determine that the efflorescences are formed by several species of secondary sulfates, chlorides and sulphur. The material from the mud are clay minerals, basically well crystallized kaolinite and minor illite-smectite mixed layer mineral, accompanied by silica minerals (opal-C, quartz, etc.) and residual anatase. The presence of TiO_2 is not new in the GCF since it has been determined previously in samples from Termas de Copahue and Anfiteatro areas, always with opal-A or opal-C.

The photograph of figure 7 shows small nests of sulphur and messy bundles of sulphate fibers form around geothermal steam escapes, and the Figure 8 shows scabs of

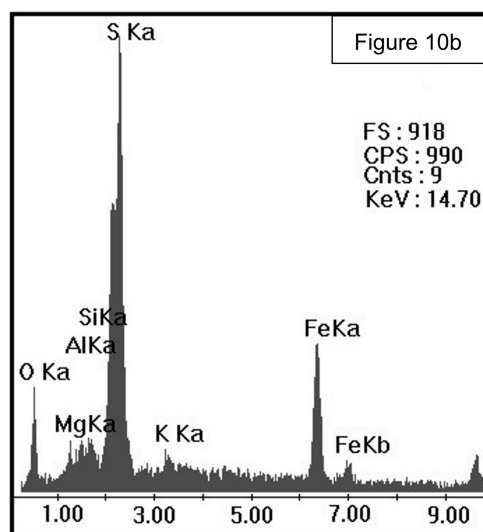
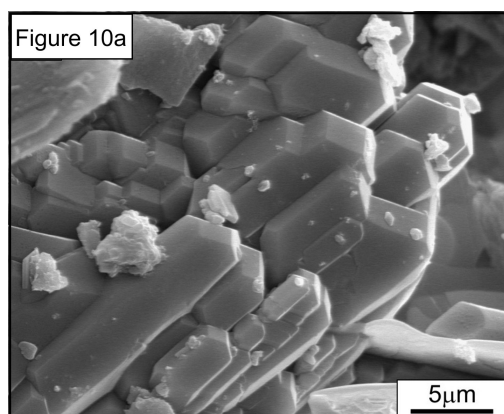


chlorides surrounding small spouts of water. Native sulphur also crystallizes as aggregates of small bladed skeletal crystals that grow around the mouths of the steam-emitting fumaroles. Sulphur is also found in the 'soils' around fumaroles and this may represent redeposited fumarolic sulphur but also it can be sulphur growing in a similar way, as vapours are emitted through the ground surface.

Alunogen, $\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$, is one of the most abundant species among the sulphate efflorescence formed as the latest products of the alteration of rocks in this area. It occurs either as white fibrous tangled masses or as prismatic parallel growths or thin platy crystals, of 8-15 μm across, that coalesces in an open cellular network. Figures 9a and 9b show the image SEM and EDX spectrum of this mineral. The white masses of alunogen darken on weathering, shrink and disappear. Alunogen is very soluble and must be returned to the local groundwater each time there is a significant rainstorm.

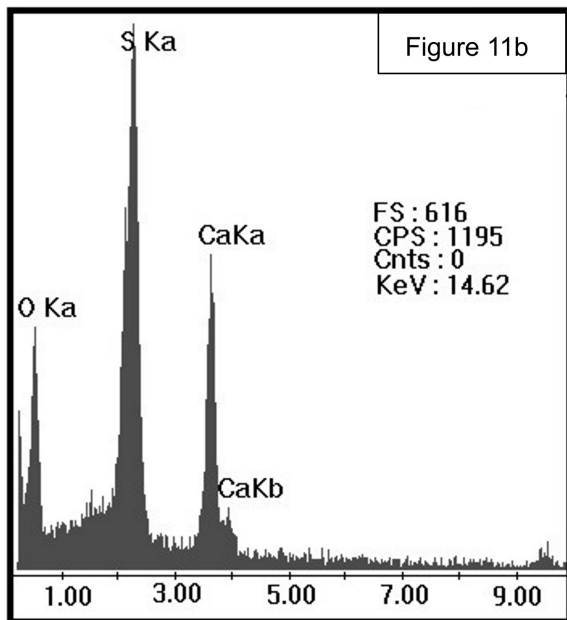
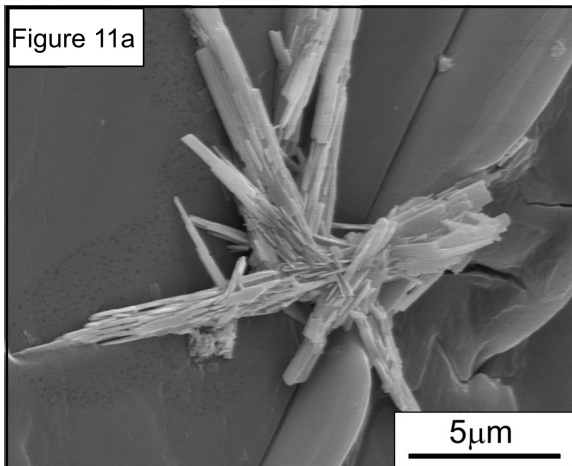


Small (<5mm diam.) spherical aggregates of radiating, acicular halotrichite, $\text{Fe}^{2+}\text{Al}_2(\text{SO}_4)_4 \cdot 22(\text{H}_2\text{O})$ and a member of the series halotriquita - pickeringite relatively richer in magnesium are also common in these efflorescence. The SEM images of these minerals show their pseudo hexagonal monoclinic habit. Figures 10a and 10b show the SEM images and EDX analysis of halotrichite and magnesium halotriquite and the RXD patterns of these minerals. The cations needed to form these minerals derive from the host rocks with the exception of sulphur that comes from H_2S gas ascending with steam.



Finally, as one of the latest minerals, it was determined the presence of gypsum in very subordinate quantities. Figures 11a and the 11b show the SEM image and the EDX

spectrum of a thin fibrous aggregate of gypsum. Among the sodium salts there were identified, by XRD and SEM, the presence of thenardita (SO_4Na_2) halite (NaCl) and potassium halite (NaKCl), also accompanied by SiO_2 and sulphur. This set of very soluble salts is dissolved each time there is a rain or the snow melts.



2. COP-2 Area

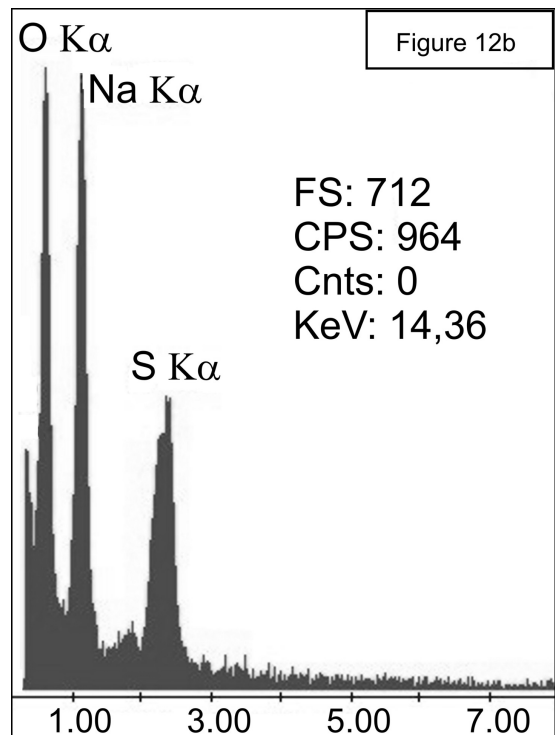
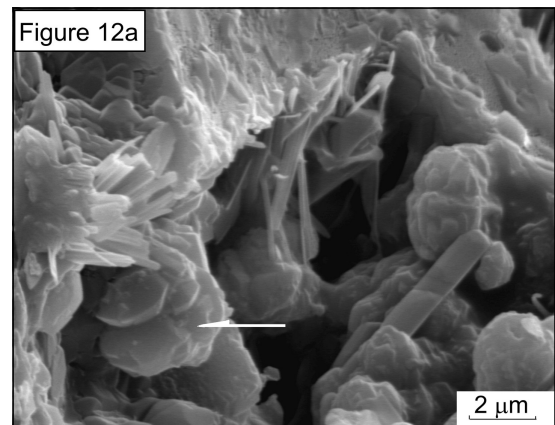
This area placed around the COP-2 well is about 2.5 km from Termas de Copahue. It is the only altered zone in Copahue that shows an important outcrop of siliceous sinter. Next to it there is an altered zone formed by a lower horizon of montmorillonite with subordinate kaolinite, quartz and C-opal, and an upper one with kaolinite with alunite and silica subordinated. The clay material is covered by an oxidized hard cap of goethite and jarosite.

The area has recently showed important mineralogical changes, all of them related with the mineral phases that are formed from the geothermal fluids: One of the most conspicuous features is the crystallization of two minerals of the sulphate-carbonate group, i.e. burkeite and hanksite, which not only have not been found before in the CGF, but they have not been mentioned before in any geothermal field. (Mas et al., 2007).

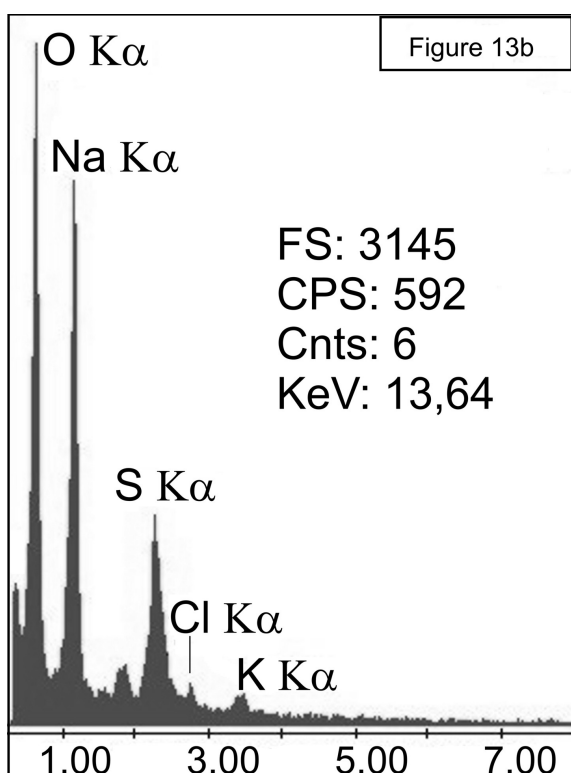
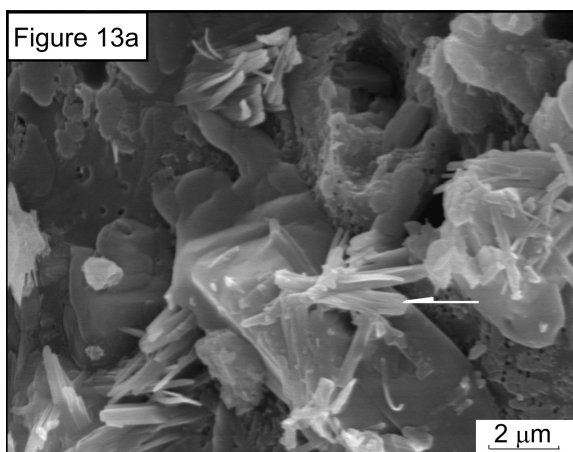
Burkeite $-\text{Na}_6(\text{CO}_3)(\text{SO}_4)_2-$, with minor hanksite $-\text{KNa}_{22}(\text{SO}_4)_9(\text{CO}_3)_2\text{Cl}-$, have precipitated as stalactite concretions around an escape of geothermal vapour in the

exterior of a pipe of the geothermal well COP-2. The translucent to opaque vuggy masses of material exhibit a massive habit with uniformly indistinguishable crystals forming large masses, and irregular protuberances over the surface. The SEM images show the presence of two superimposed different materials. One of them, the most abundant, forms a substrate of tabular crystals of $0.5 \times 3 \times 8 \mu\text{m}$ of size. Sheaves of thin and long crystals with hexagonal section, of about $5 \mu\text{m}$ of length, lay over the tabular crystals. The SEM photomicrography's of the Figures 12a and 13a show both minerals in detail.

The chemical compositions of the minerals were controlled by means of an energy-dispersive probe incorporated to the electron microscope. Figures 12b and 13b show the spectra of each one. The spectrum of figure 12b corresponds to the tabular mineral of the substrate, and it indicates the presence of Na, S, C and O; while the spectrum of the figure 13b corresponds to the fibrous radiated sheaves, and shows the peaks of C, S, Cl, O, Na and K. The elements identified in the EDXS spectrum coincide with the mineral determination carried out by DRX.



Hanksite has been found also as precipitated scabs in a side of the flange of the COP-4 well, about 900 m of COP-2, and in the same alteration area, accompanied by poorly crystallized SiO_2 and tinalconite.



This last mineral is also a new mention for Copahue. It has been identified by X-ray powder diffraction (XRD) analysis using a Rigaku Dmax IIC automatic powder diffractometer with JADE v.7 analysis software. Copper $K\alpha$ radiation was used, and the $K\alpha_2$ contribution was stripped by a graphite monochromator. The powder XRD patterns were made over a diffraction-angle (2θ) range of 3° to 60° , with a step size of 0.02° and a counting time of 1s per step. The minerals were determined by comparing the powder patterns obtained with those in the JCPDS powder diffraction files (PDF). The interplanar spaces are very close to tinalconite.

Tinalconite is a mineral that is closely related to and often intimately associated with the mineral borax. Most old mineral specimens of borax are chalky white due to a chemical reaction from dehydration (Anthony et al. 2003). The formula of tinalconite can be written as: $Na_2B_4O_5(OH)_4 \cdot 3H_2O$. This formula is technically identical to the formula that is generally used for tinalconite, $Na_2B_4O_7 \cdot 5H_2O$. However the alternative formula reflects the ionic interaction of the hydroxides in the structure as opposed to a more passive role for the unbonded water molecules. The basic structure of tinalconite contains chains of interlocking $BO_2(OH)$

triangles and $BO_3(OH)$ tetrahedrons bonded to chains of sodium and water octahedrons.

Minerals that are the result of human intervention are sometimes not considered true minerals by mineralogists. Tinalconite, however, is not exclusively an alteration product of borax dehydration after the borax has been excavated. The mineral has been found as a naturally occurring secondary mineral at Searles Lake, California, the mineral's type locality (Pemberton, 1975). These specimens of cryptocrystalline aggregates are the result of dehydration of borax crystals that had been exposed to the dry air conditions at the site. In addition though, primary tinalconite crystals have been mentioned there in drill cores forming well shaped di-rhombohedral pseudo-octahedral crystals.

In Copahue, tinalconite seems to be also a primary phase because it occurs with hanksite, and both are precipitating from the saturated geothermal vapour fluids. Besides, borax has not been found in this locality, although sassolite (H_3BO_3) had been previously described in the pipes of the geothermoelectric plant placed next to the geothermal well COP-1, as a porous white material, fragile and very soft to the tact, which was precipitate during winter's months as inlay and scaling in the pipes. Recently this mineral also has been found as soft concretions around an escape of geothermal vapour in the exterior wall of a pipe in COP-2 well.

DISCUSSION AND CONCLUSIONS

The volcanic complex that constituted the CGF is affected by a fault system which main direction is N55W with their associated directions, N55E, EW and N40W. The geothermal reservoir is located predominantly in zones of secondary permeability of the calc-alkaline lavas and pyroclastic rocks of Las Mellizas Formation, and contains overheated steam.

The feasibility of the geothermal resource in this field was analyzed by JICA-EPEN (1993) study and the mineralogical and geochemical characteristics of the geothermal field were determined by Mas (1993). Mas et al. (2000) analyzed the distribution of heat flow in the system.

In the active hydrothermal areas of Copahue there are widespread evidences that hydrothermal minerals are deposited directly from the geothermal fluid or from water-rock interactions.

The recent formation of mud pots and the important fumarolic activity observed in an area over a talus adjacent to Termas de Copahue, indicate that this area has become a very active geothermal zone.

X-ray powder diffraction, electron microprobe analyses and classical optical methods were used to identify these hydrothermal minerals. Sulphates (alunogen, halotrichite, etc.), clay minerals (kaolinite, illite-smectite mixed layer mineral, etc.) and silica minerals (opal, and quartz) are the dominant phases. Native sulphur and pyrite are next in order of abundance. Some zeolites are also present.

In COP-2 area two minerals of the carbonate-sulphate group, burkeite and hanksite, besides tinalconite, are nowadays forming from the geothermal fluids that reach to the surface.

These facts point out that some changes in the physico-chemical conditions of the field are been taken place. These changes may be related to:

- the continue operation of the COP-1 for a lapse of 20 years and the exploitation, now interrupted, of COP-2 and COP-3 during about 10 years, would have caused the falling down of pressure in the upper zone of the reservoir. This fact, however, seems to be *a priori* rather improbable, for the production parameters of the wells up to the moment do not show important differences with the reported data from previous reservoir studies, or
- the Copahue Volcano activity would have generated structural as well as physico-chemical variations in the reservoir conditions as a stage in the activity increment it has suffered in the last sixteen years as shown in the three eruptive episodes. This may have caused the reactivation of the fractures system that control the reservoir, both in the zone around the wells COP-1, COP-2 and COP-3 and in Termas de Copahue leading to a pressure disequilibrium that led to the mentioned changes. This hypothesis seems to be the more firm and it would explain the observed changes. Nevertheless more studied are needed to arrive a solid conclusion.

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REFERENCES

Anthony, J.W., Bideaux, R.A., Bladh, K.W., and Nichols, M.C. 2003: Handbook of Mineralogy, Volume V. Borates, Carbonates, Sulfates. Mineral Data Publishing, Tucson, AZ, 813 pp.

JICA-EPEN 1992. The Feasibility Study on the Northern Neuquén Geothermal Development Project. Final Report. Ente Provincial de Energía del Neuquén. Japan International Cooperation Agency (inédito).

Mas, L. 1993. El Campo Geotérmico Copahue: Los Minerales de Alteración y las Inclusiones Fluidas como Indicadores de los Parámetros Físico-Químicos del Sistema. Tesis Doctoral. Biblioteca Central UNS. Bahía Blanca. (ined.).199 pp.

Mas, G.R.; Mas, L.C. & Bengochea, A.L.; 1996. Hydrothermal Surface Alteration in the Copahue Geothermal Field, Neuquén Province, Arg. Geothermal Reservoir Engineering.; 241-246. ISSN 1058 2525; Stanford California. USA.

Mas, L.C.; G.R. Mas & L. Bengochea; 2000: The heat flow distribution and its relation with the tectonic scheme of the Copahue Geothermal Field. World Geothermal Congress 2000. 1419-1424. Japón.

Mas, G.; Bengochea, L. & Mas, L.C. 2007: Burkeite and Hanksite in Copahue, Argentine. First occurrence of sulphate-carbonate minerals in a Geothermal Field. Mineralogical Magazine, 71(2): 235-240.

Mas, G.R., L. Bengochea & L.C. Mas (1998): Sassolita de Neoformación en Pozos Geotérmicos de Copahue. Minmet' 98. IV Reunión de Mineralogía y Metalogenia. 179-183; Bahía Blanca. 23-25 de septiembre 1998.

Pemberton, H.E. (1975): The crystal habits and forms of the minerals of Searles Lake, San Bernardino County, California. Mineralogical Record 6 (2): 75-83.

Pesce, A., 1989. Evolución Volcano-tectónica del Complejo Efusivo Copahue-Caviahue y su modelo Geotérmico Preliminar. Revista de la Asociación Geológica Argentina. 44(1-4): 307-327