

DATING K-RICH FINE-GRAINED PHYLLOSILICATES FROM MAFIC LITHOLOGIES. AN APPROACH TO CONSTRAIN THE TIMING OF LOW-TEMPERATURE PROCESSES IN CENTRAL ANDES

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INTRODUCTION

K-rich fine-grained ($< 2 \mu$) phyllosilicates are usually used to date diagenetic to very low-grade processes in clastic sediments (e.g. Srodon, 2002; Rousset & Clauer, 2003, Belmar et al., 2004 and references therein). Among phyllosilicates, illite are the most used minerals to constrain age by the K-Ar methodology, based on its formation during burial diagenesis and retention of Ar by small crystals, allowing this system as effective isotopic clock. Nevertheless, some other K-rich fine grained phyllosilicates as glauconite, sericite or celadonite can be formed during secondary very low to low-temperature secondary processes in mafic systems. $^{40}\text{Ar}/^{39}\text{Ar}$ dating of fine grained glauconite and sericite could evidence loss of ^{39}Ar by recoil giving disturbed spectra without geological significance (e.g. Foland et al., 1992).

In the Andes of central Chile, mafic volcanic-rich lithologies dominated and under this context, the mechanism to grown illite minerals could be different from those in clastic sediments and, consequently, K-Ar ages obtained from these type of rocks could be controversial. $^{40}\text{Ar}/^{39}\text{Ar}$ dating of highly sericitized plagioclase by the step-heating procedure has been evidence as an optimal approach to dating the very low-grade metamorphism (Aguirre et al., 1999; Fuentes et al., 2005). Also, $^{40}\text{Ar}/^{39}\text{Ar}$ dating quart-sericite fine-grained aggregates seems to be useful to constrain sericite alteration events in epithermal ore deposits (Arancibia et al., 2006b).

The aim of this research is to evaluate the ability of date by the K-Ar methodology celadonite and illite developed during low-temperature secondary processes in mafic lithologies. The significance of the obtained ages could be of great relevance in the temporal interpretation of low-temperature fluid-rock interaction.

MATERIALS AND METHODS

Celadonite $[\text{K}(\text{Fe}^{3+}, \text{Al}^{3+})(\text{Mg}^{2+}, \text{Fe}_2^{2+})\text{Si}_4\text{O}_{10}(\text{OH})_2]$, an iron-rich dioctahedral mica, is typically present as infillings in veins, vesicles or some other open spaces in basaltic lavas during low-temperature alteration together quartz, calcite, zeolites and other clay minerals (e.g., Loveland and Bendelow, 1984; Gallahan and Duncan, 1994).

For the purpose of this study, celadonite was firstly recognised under petrographic microscope and then carefully studied under XRD and SEM-EDS. Samples selected for K-Ar dating belong to different Mesozoic units from both the Coastal Range and the Andes (samples MBTF-) along different latitudes (Table 1). In most cases, celadonite appear as a thin film in the outer rim of amygdules (Fig. 1), intimately intergrown with chlorite and mixed-layer chlorite/smectite as previously described by Belmar et al. (2001).

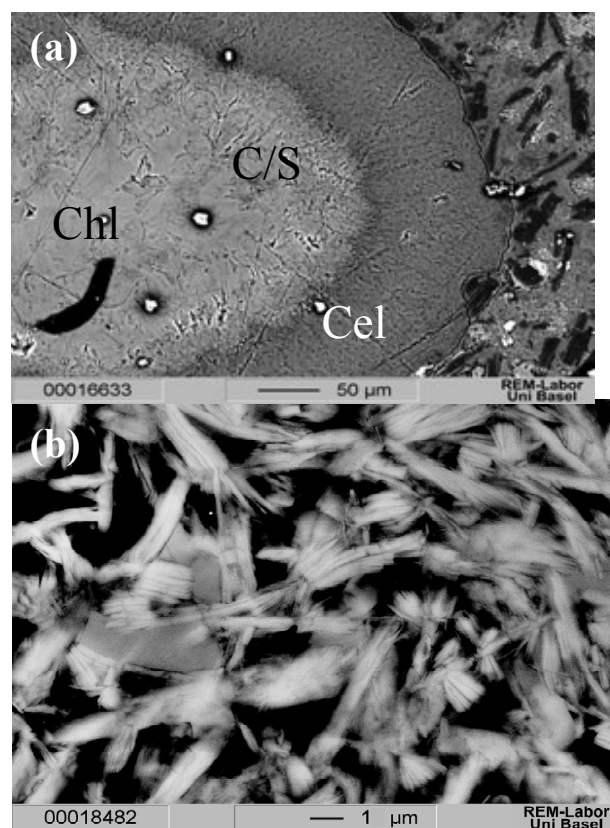


Figure 1. (a) Back-scattered image of amygdule in andesitic lava showing the intimate relationships between celadonite (Cel), chlorite (Chl) and mixed layer chlorite/smectite (C/S). (b) Detail of celadonite crystals.

Concentrate of < 2 μ clay minerals from the groundmass of tuffs and volcanoclastic rocks were also selected for dating (Table 1). In these samples, mineral identification was carried out by oriented powdered XR-diffraction.

Separation of clay minerals was carried out by traditional < 2 μ clay separation. Hand-picking under binocular microscope were also used for some celadonite. K was analysed by atomic absorption and radiogenic Ar by mass spectrometry after extraction of gas from sample by

furnace melting at the Geochronological Laboratories of the SERNAGEOMIN (see more methodological details in Duhart et al., 2001). SEM and EMPA data were obtained in a Jeol JXA-8600 SEM (Basel University, Switzerland) and a SEM-Probe CAMEBAX SU-30 (Universidad de Chile, Chile). Results of the K-Ar experiments are present in Table 1, together with the assumed age of the host rock. All ages are given with the 2 σ error.

Table 1.- K-Ar ages in fine-grained phyllosilicates. In bold, mineral used for dating.

| SAMPLE | LOCATION (UTM E,N Coord.) | PETROLOGICAL CHARACTERISTICS | ASSUMED PRIMARY AGE | K-Ar Age (Ma) |
|-----------|------------------------------|---|--------------------------|------------------|
| ARQ01-49 | 318448, 6692245 | Andesitic lava flow with amygdule and veins with celadonite and calcite. | 110 | 93 \pm 2 |
| QLT04-17A | 339946, 6395984 | Andesitic lava flow with amygdule and veins with celadonite . | 100-105 | 100 \pm 3 |
| MLP02-17 | 312779, 6255894 | Andesitic tuff with celadonite in the groundmass. | 125 | 98 \pm 3 |
| MBTF-7 | 368363, 6130721 | Basaltic lava flow with amygdule. Vesicles commonly zoned with thin films of celadonite at the rim and quartz to the centre. | 31-37 | 15.0 \pm 1.6 |
| MBTF-14 | 348324, 6150422 | Basaltic lava flow with celadonite ion amygdules. | “ | 22.6 \pm 1.1 |
| MBTF-1 | 370725, 6130802 | Andesitic lava with amygdule and veins with celadonite . | Middle-Upper Jurassic | 101.3 \pm 2.9 |
| MBTF-22A | 370405, 6131233 | Andesitic lava with amygdule and veins with celadonite and chlorite. | “ | 108 \pm 4 |
| MBTF23E | 370453, 6131152 | Andesitic lava with amygdule and veins with celadonite and chlorite. | “ | 105 \pm 3 |
| MBTF-24 | 366822, 6133913 | Volcanic breccia with celadonite in the matrix. | 31-37 | 22.8 \pm 1.8 |
| MBTF-34 | 360541, 6136761 | Tuff with amygdules of celadonite and chlorite. | “ | 16.3 \pm 0.8 |
| MBTF-35 | 360655, 6136450 | Tuff with amygdules of celadonite and chlorite. | “ | 19.1 \pm 0.8 |
| QLT03-11 | 336637, 6374310 | Ignimbrite with illite in the groundmass. | 105-110 | 83 \pm 2 |
| QLT04-21 | 340244, 6397623 | Tuff with illite in the groundmass. | 100-105 | 53.2 \pm 1.3 |
| QLT04-20 | 340506, 6397034 | Tuff with illite in the groundmass. | “ | 65 \pm 2 |
| QLT04-23 | 338112, 6404661 | Conglomerate with illite in the groundmass. | “ | 64 \pm 2 |

With the aim to check the ability of use celadonite for $^{40}\text{Ar}/^{39}\text{Ar}$ dating, selected fine-grained aggregates were also analysed at the SERNAGEOMIN according the methodology described in Arancibia et al. (2006a). Results of are in Fig. 2.

DISCUSSION AND CONCLUSIONS

Celadonite is assumed to be formed under very low-temperature fluid-rock interaction (< 60°C, Duplay et al., 1989; Gallahan and Duncan, 1994) but can rest stable to high temperature (\approx 400°C; Velde 1972). Nevertheless, no data are published in the literature concerning its temperature closure. Because celadonite has a crystallographic ordering of white-micas (structure 1M according Wise and Eugster, 1964), and due its very small

crystal size, closure temperature around 200°C could be a realistic value for this mineral.

According this assumption, K-Ar ages obtained from celadonite in andesitic and basaltic lava flows could indicate the timing of secondary alteration processes affecting them. In fact, samples MBTF- with K-Ar celadonite ages of 101-108 Ma belong from andesitic lava flows, metamorphosed on the prehnite-pumpellyite facies, of the *Río Damas Formation*, of Middle-Upper Jurassic age based on palaeontological data (Belmar et al., 2003). Samples MBTF- with K-Ar ages from 15-23 Ma belong from andesitic and volcanoclastic rocks, metamorphosed on the high-T zeolite facies, of the *Coya-Mayali Formation* (Eocene-Oligocene, Belmar et al., 2003). Both set of samples belong from the Andean belt in central Chile and constrain the time-interval between volcanism and very

low-grade metamorphism in ≈ 45 Ma and ≈ 15 Ma to achieve the prehnite-pumpellyite (in the Jurassic rocks) and zeolite facies (in Tertiary rocks), respectively.

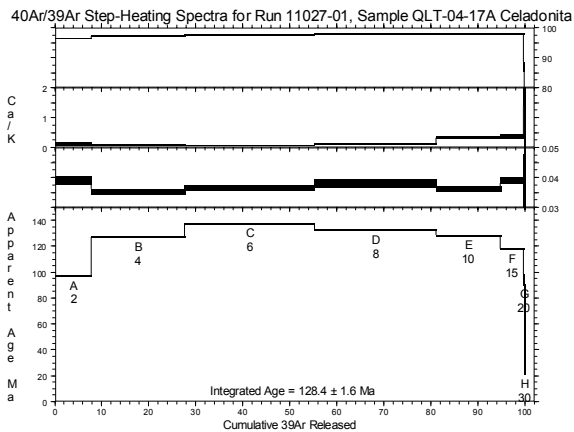


Figure 2. Conventional age spectra of sample QLT04-17A showing typical recoil pattern probably by loss of ^{39}Ar due to the very fine-grain of celadonite ($< 1\mu$) crystals.

Samples ARQ01-49 and MLP02-17 belong from the Coastal Range at the latitude of La Serena and south of Santiago, respectively. In both outcrops, celadonite is in close relationship with Cu stratabound ore deposits (see Carrillo-Rosúa et al., 2006). Host rocks (*Arqueros Formation* and *Lo Prado Formation*, respectively) were metamorphosed in the high-T zeolite to prehnite-pumpellyite and prehnite-pumpellyite facies, respectively, indicating a time interval of ≈ 15 Ma and ≈ 25 Ma between volcanism and metamorphism.

Samples QLT04- belong from a same outcrop of the *Las Chilcas Formation* in the Coastal Range of central Chile, with assumed age (based on stratigraphic relationships) of 100-105 Ma. In this outcrops only mafic phyllosilicates, quartz, calcite and rare zeolite are present as secondary minerals. K-Ar age from celadonite in sample QLT04-17A of 100 ± 3 could be them considered as indicative of post-magmatic very low-temperature hydrothermal circulation during the first stage of subsidence of the Mesozoic basins. Unfortunately, the $^{40}\text{Ar}/^{39}\text{Ar}$ spectra during the incremental-heating experiment loss of ^{39}Ar by recoil without development of a plateau age, giving a meaningless

spectrum. Moreover, the spectrum obtained is similar to the spectrum for the SED-2 sericite of Foland et al (1992), interpreted by these authors as consequence of $^{40}\text{Ar}/^{39}\text{Ar}$ heterogeneities due to ^{39}Ar redistribution (for example from high- to low-K regions or grains) during irradiation.

The three QLT04- samples on which illite is used for dating present a different behaviour. These samples are located in the same cross section, belonging from the same geological unit, and placed several hundred of meters away from sample QLT04-17A. K-Ar from the illite-rich $< 2\mu$ fraction in three samples range from 53 to 65 Ma, younger than the K-Ar age of 100 ± 3 Ma obtained from celadonite. A probable explanation for these younger ages could be in relation with the mechanism to develop illite in mafic systems. In this case, illite could be in relation with local hydrothermal alteration related with the epizonal emplacement of Paleocene intrusives rather than with secondary processes related with the regional very low-grade metamorphism affecting the Mesozoic sequences.

Finally, sample QLT03-11 belong from an ignimbrite from the *Las Chilcas Formation*, with assumed age of 105-110 Ma (based on stratigraphic relationships). The K-Ar age of 83 ± 2 Ma must be also interpreted in terms of secondary alteration related to local plutonic activity rather than regional metamorphism.

In conclusion, K-Ar dating of celadonite in mafic volcanic and volcanoclastic systems is an optimal approach to constrain the secondary low-T processes affecting them. Nevertheless, K-Ar dating of other fine-grained K-rich phyllosilicates (e.g. illite) in these mafic systems, could give ages without regional significance due to (i) the mechanism of illite grown in mafic systems and (ii) the facility of develop illite in the groundmass of volcanoclastic rocks during local alteration processes.

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RESUMEN

La fracción fina ($< 2 \mu$) de filosilicatos ricos en K (celadonita e illita) presente en litologías máficas (flujos de lava y tobas) de los Andes de Chile central se ha utilizado para ser datadas mediante K-Ar, con el objetivo de constreñir la edad de los procesos de interacción secundarios fluido-roca de baja temperatura. La celadonita aparece principalmente como finas películas en las paredes de amígdalas o en la masa fundamental, en íntima relación con clorita e intercrecimientos clorita/esmectita. La illita aparece, fundamentalmente, en la masa fundamental de rocas volcánicas. La datación K-Ar en celadonita en sistemas volcánicos y volcánoclasticos máficos ha resultado ser un método idóneo para datar estos eventos de alteración secundarios de baja temperatura. Sin embargo, la datación en illitas en esos sistemas puede dar como resultado edades sin significado regional por: (i) los mecanismos de crecimiento de la illita en estos sistemas máficos y (ii) la facilidad para que se desarrolle illita en la masa fundamental de rocas volcánoclasticas como resultado de otros procesos de alteración de índole local.