Applied Clay Science 134 (2016) 235–245

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

Hydrothermal alteration of chlorite to randomly interstratified corrensite-chlorite: Geological evidence from the Oligocene Smrekovec Volcanic Complex, Slovenia

Polona Kralj

Geological Survey of Slovenia, Dimičeva 14, SI-1000 Ljubljana, Slovenia

ARTICLE INFO

Article history:
Received 31 March 2016
Received in revised form 8 October 2016
Accepted 16 October 2016
Available online 31 October 2016

Keywords:
Volcanic-hydrothermal alteration
Chlorite
Chlorite-smectite
Corrensite-chlorite
Zeolites

ABSTRACT

Chlorite, ordered mixed-layer chlorite-smectites, laumontite, quartz and albite are the most widespread alteration assemblage in cone-building and near-vent successions of lavas, autoclastic, pyroclastic and resedimented volcaniclastic deposits of the Oligocene Smrekovec Volcanic Complex, Slovenia. Randomly interstratified corrensite-chlorite with ~70–80% of corrensite layers (R0 Cr-Ch) is less common in occurrence and associated either with clinoptilolite and heulandite in fine-grained vitric tuffs, or with prehnite, laumontite, actinolite, analcime and albite in extensively altered and/or fractured host-rocks. The assemblage with clinoptilolite and heulandite indicates the temperatures of formation of <~120 °C and can be regarded as intermediate in the prograde alteration process of volcanic glass that leads in progressively increasing temperature regime to the formation of chlorite, laumontite, prehnite and albite. The assemblage of R0 Cr-Ch, prehnite, laumontite and actinolite developed in different superimposed temperature regimes and/or stages of hydrothermal activity related to the emplacement and subsequent gradual cooling of the Kramarica Sill. The formation of prehnite and actinolite signifies the highest-temperature conditions attaining up to ~300 °C. Laumontite and R0 Cr-Ch extensively developed during the cooling period and as a result of the incursion of alkaline Ca-Mg hydrothermal fluids that possibly evolved from deep ground-waters convecting through Triassic dolomite in the basement of the submarine Smrekovec stratovolcano-hosted hydrothermal system.

1. Introduction

Clay minerals and zeolites are widespread alteration products of volcanic material deposited on the Earth's surface or buried at shallow crustal depths (Henley and Ellis, 1983; Wohletz and Heiken, 1992; Reyes et al., 1993; Velde, 1995; Hillier et al., 2006; Wilson, 2013). Particularly favourable geological environments are volcanic-hydrothermal systems where locally elevated geothermal gradients and hydrothermal activity driven by convection accelerate the alteration processes. The processes are complex and depend on many factors the most important being chemical composition, porosity and permeability of the host-rock, temperature, chemical composition, source, pathways and mixing processes of reacting fluids, availability of magmatic gases, duration of hydrothermal activity, superimposed regimes, hydrology of the system and tectonic activity (Hennenberger and Browne, 1988; Reyes, 1990; Hochstein and Browne, 2000). Evolution of volcanic-hydrothermal systems from early to mature stage is reflected in temporal sequences of crystallisation of alteration minerals (Rigault et al., 2010).

In the early stage of hydrothermal activity, acidic fluids predominate and typical newly-formed clay minerals are halloysite, kaolinite and pyrophyllite (Inoue, 1995). In the mature stage, nearly pH neutral alkaline and alkaline earth chloride fluids commonly evolve and early reactions with host-rock produce smectites. Depending on the activity of potassium, calcium and magnesium ions and temperature regime they transform to mixed-layer illite-smectites (I-Sm) and/or chlorite-smectites (Ch-Sm), and eventually, to illite and/or chlorite (Utada, 2001; Reyes, 2000). Various compositional series of Ch-Sm have been recognised world-wide in host-rocks of basaltic to andesitic composition, from randomly interlayered R0 Ch-Sm with varying proportions of chlorite and smectite layers to ordered R1 varieties including tosudite, corrensite and mixed-layer chlorite-corrensite (Ch-Cr) (Inoue and Utada, 1991; Bettison-Varga et al., 1991; Hillier, 1993; Schiffman and Staudigel, 1995; Niu and Yoshimura, 1996; Bettison-Varga and Mackinnon, 1997; Murakami et al., 1999; Mojares et al., 2000; Robinson et al., 2002).

Mixed-layer minerals intermediate between corrensite and chlorite have been studied by Shau et al. (1990) and Shau and Peacor (1992) using transmission electron microscopy (TEM) and analytical electron microscopy (AEM). Hillier (1993) has shown that any X-ray diffraction (XRD) pattern of maximum ordered R1 mixed-layer chlorite-smectite has an exact equivalent randomly interstratified smectite-corrensite or chlorite-corrensite. The difficulty of identification of actual fundamental layers in such interstratified chlorite minerals is shown by the effect of

E-mail address: polona.kralj@geo-zs.si.

http://dx.doi.org/10.1016/j.clay.2016.10.025

segregation of layer types into the layer arrangement. In a randomly interstratified chlorite-corrensite the effect of partial segregation of chlorite and corrensite layers on the diffraction pattern of an ethylene glycol solvated sample is to produce the high d-value (001) reflection near 31 Å (Hillier, 1995).

Chlorite, R1 Ch-Sm with ~60–90% of chlorite layers and zeolites are the most widespread authigenic mineral assemblage in volcanic successions of the Oligocene Smrekovec Volcanic Complex (SVC) developed as a result of hydrothermal alteration. Randomly interstratified corrensite-chlorite with ~70–80% of corrensite layers (R0 Cr-Ch) is associated either with clinoptilolite and heulandite in fine-grained vitric tuffs or with prehnite, laumontite, actinolite, analcime, and albite (replacing pyrogenetic plagioclases and volcanic glass) in extensively altered and fractured rocks. The aim of the present contribution is to explain the geological occurrence and possible physical and geochemical determinants in the volcanic-hydrothermal system that caused the formation of R0 Cr-Ch.

2. Sampling and analytical methods

The sampling was performed in three segments of the sections Krnes-1, Travnik-1 and Roma-34 (Fig. 1) attaining 215 m, 170 m and 252 m, respectively. The main criterion was the change in lithofacies (Figs. 2 and 3, see the columns Sampling), although in very coarse grained, fractured or extensively altered rocks with abundant cement and vein minerals, several samples were commonly taken from a single lithofacies in order to obtain more reliable composition of authigenic minerals. For detailed studies of clay minerals and zeolites, 83, 43 and 96 samples have been selected from the sections Krnes-1, Travnik-1 and Roma-34, respectively.

Standard X-ray diffraction (XRD) techniques were applied to determine the mineral content of whole-rock powdered samples and slurries dispersed on glass slides to orient the clays. The analysis was performed using a Philips diffractometer PW 3719 and a goniometer PW 1820, owned by the Department of Geology, Faculty of Natural Sciences and Technology, University Ljubljana. Machine settings for all analysed samples were as follows: generator operated at 40 kV and 30 mA using CuK_{α} radiation (wavelengths $K_{\alpha 1} = 1.54056$ Å and $K_{\alpha 2} = 1.54439$ Å), Ni filter, with automatic divergence slit and monochromator on. Scanning rate was 2°2θ/min; scanning range amounted to 2°2θ − 70°2θ for powdered samples and 2°2θ–45°2θ for oriented samples. Digital data were processed using peak-fitting program X'Pert HighScore Plus 4.0. Semi-quantitative analysis was performed by the program using the data base, internal standard rock-samples and bulk chemical composition of powdered samples.

Mineral composition of clay fraction of volcanic and volcaniclastic rocks was determined on oriented samples. Whole-rock samples were powdered and the <2 μm fraction separated from a slurry by centrifugation. Air-dried, ethylene glycol solvated, thermally treated (375 °C, 500 °C) and Mg-saturated samples were analysed. Estimation of the amount of expandable layers in the crystal structure of Ch-Sm minerals is based on expansivity of $(00l)_c/(00l)_s$ reflections in response to ethylene glycol solvation (001/001 versus 002/002 for Hower, 1981; 002/002 versus 004/005 for Reynolds, 1980).

Petrographic data were obtained from optical examination of 197 thin sections. Detailed studies of retrograde and overprinting reactions were performed on 9 polished thin sections using a scanning electron

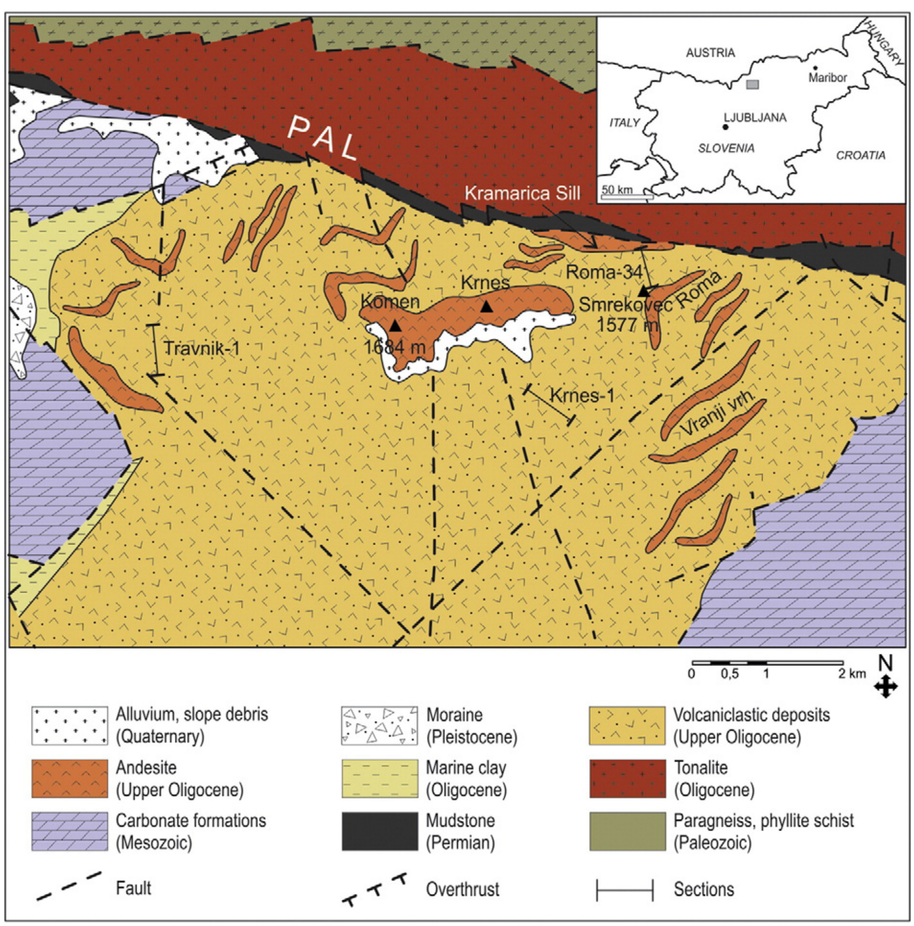

Fig. 1. Geological map of the northern sector of the Smrekovec Volcanic Complex (after Mioč, 1983 and Buser, 2009) characterised by hydrothermal alteration, the position of the studied sections Travnik-1, Roma-34 and Krnes-1 and a sketch showing geographic position of Slovenia and the study area.