



CONSTRAINING VERY LOW-GRADE METAMORPHIC CONDITIONS BASED ON PREHNITE CHEMISTRY

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INTRODUCTION

Prehnite $[\text{Ca}_2(\text{Al,Fe}^{3+})_4(\text{Si,Al})_8(\text{OH})_2]$, together with epidote and pumpellyite, is one of the most common calc-silicates present in very low to low-grade metabasites. Prehnite is typically present filling open spaces (vugs, veins, fissures and amygdules), replacing primary minerals (mostly Ca-rich plagioclase) and in the groundmass of volcanic rocks. P-T conditions of prehnite formation are shown in the petrogenetic grid of Frey *et al* (1991) with temperature ranging between 190-320°C and a maximum pressure of 4 kbar. Additionally, some studies show a relation between the Fe/(Fe+Al) ratio in prehnite and the metamorphic grade (Beierdorsfer & Day, 1995). Here we present the chemistry of prehnites from very low-grade metabasalts from the Lower Cretaceous of the Coastal Range in north-central Chile, at the latitude of La Serena ($\approx 30^\circ\text{S}$). The combination of major, trace elements, and Sr isotopic signatures of these prehnites, together with the mineral chemistry of associated minerals would be used to constrain the metamorphic conditions.

GEOLOGICAL FRAMEWORK

The Lower Cretaceous volcanism at the La Serena region is represented by porphyritic to highly porphyritic high-K calc-alkaline andesitic basalts of the *Arqueros* and *Quebrada Marquesa* formations (Morata & Aguirre, *in press*). These lavas are homogeneous in composition, with plagioclase ($\approx \text{An}_{61}\text{Ab}_{37}\text{Or}_2$), calcic clinopyroxene ($\approx \text{Wo}_{41}\text{En}_{42}\text{Fs}_{17}$) and minor altered olivine and Ti-magnetite as phenocrysts. $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology on plagioclase gave ages of 117-115 Ma for lavas of the *Arqueros Formation*. An age of 110 Ma is assumed for the lavas of the *Quebrada Marquesa Formation* based on stratigraphic relationships. The geochemical signature of these Lower Cretaceous lavas is typical of magmas generated in subduction zones, with LILE enrichment and Nb-Ta depletion. Isotopically, they are characterized by a low and highly homogeneous $(^{87}\text{Sr}/^{86}\text{Sr})_0$ of *c.* 0.7036 and a positive ϵNd value of +2.9 to +4.7, and $(^{143}\text{Nd}/^{144}\text{Nd})_0$ of *c.* 0.5127. Based on geochemical data, an intra-arc extensional setting has been proposed by Morata & Aguirre (*in press*) during the genesis of these lavas.

METAMORPHIC MINERALOGY

Metamorphic minerals are present in selected metadomains: (i) as pseudomorphs of primary igneous minerals, with presence of sericite and albite, with minor prehnite and calcite, as replacement of Ca-plagioclase, and chlorite, magnetite, and rare pumpellyite (Fig. 1a) as

replacement of olivine; (ii) in the groundmass, with development of mafic phyllosilicates; and (iii) filling open spaces (vesicles and fissures), with abundant prehnite (some crystals up to 2 cm in size), calcite, small acicular crystals of pumpellyite, and idiomorphous hydrogarnet (hydrogrossular) (Fig 1b) together with chlorite, epidote and albite.

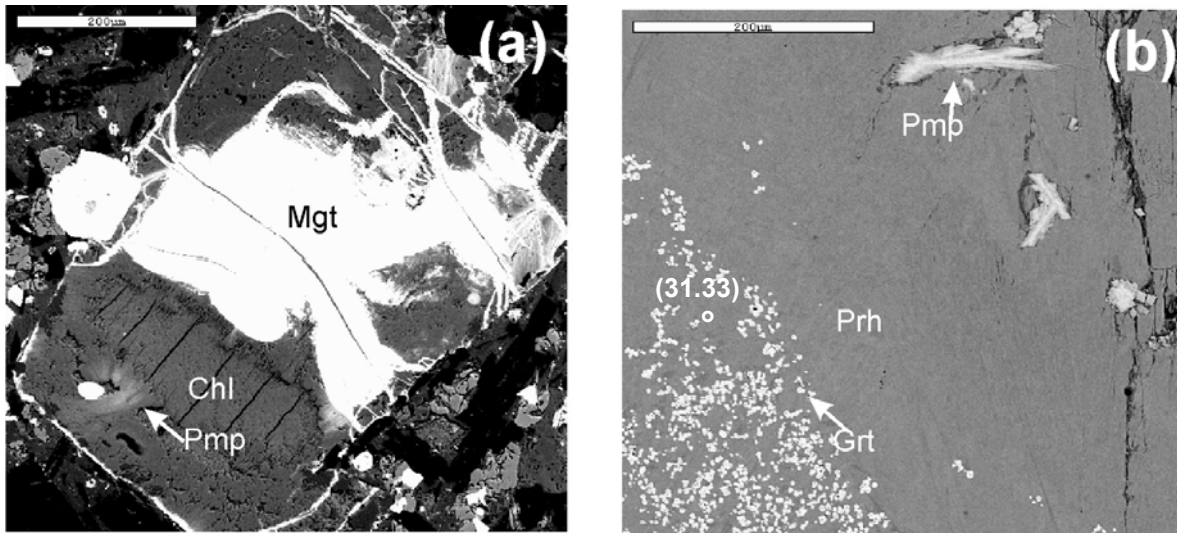


Figure 1.- Back-scattered electron images obtained in a Zeiss DSM 950 scanning electron microscope (Centro de Instrumentación Científica de la Universidad de Granada) of the metamorphic minerals present in the Lower Cretaceous volcanic rocks of the Coastal Range at the La Serena ($\approx 30^{\circ}\text{S}$) region. (a) Olivine phenocryst replaced by magnetite (Mgt), chlorite (Chl) and pumpellyite (Pmp). (b) Prehnite (Prh) filling an amygdale from a volcanic rock, together with acicular pumpellyite (Pmp) and tiny idiomorphous hydrogrossular (Grt). In parentheses, values of $X\text{Fe}^{3+}$ in prehnite obtained from EDX-SEM.

The paragenesis of prehnite + pumpellyite, together with albite and chlorite, is typical of the prehnite-pumpellyite facies, with P-T stability of 200-270°C and $P < 4$ kb. Temperatures obtained for the chlorite using Cathelineau's (1988) geothermometry are in the range 180-240°C. Experimental work on prehnite, epidote and hydrogarnet (Liou et al., 1983) indicates a minimum temperature of *c.* 340°C for hydrogarnet, slightly decreasing with increasing oxygen fugacity, and almost independent of pressure. On the other hand, according to Rossman & Aines (1991) and Anthauer & Rossman (1998), the water content of hydrogarnet increases with a decrease in temperature and/or pressure. In our case, the H_2O calculated (up to 3.5 wt%) in the hydrogarnet paragenetic with prehnite is consistent with low P-T values.

No data are available for the age of this metamorphism. However, assuming a time-interval between magmatism and metamorphism of *c.* 25 Ma to reach the prehnite-pumpellyite facies (according to the results in Aguirre *et al.*, 1999), an age of *c.* 90 Ma can be estimated for this metamorphism.

PREHNITE CHEMISTRY

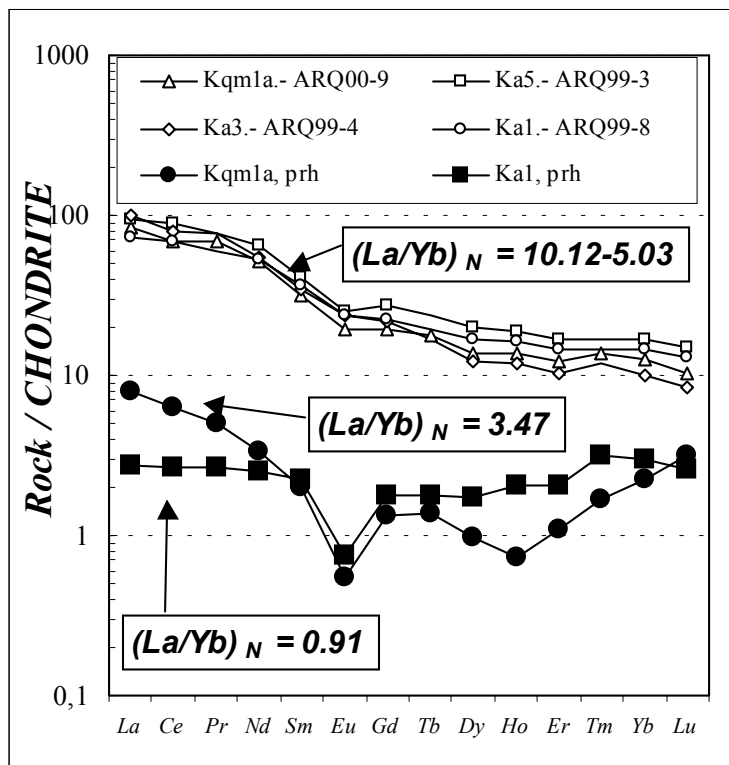
Prehnite from centimetric vesicles and/or fissures were selected for an integrated SEM-EDX-ICPMS-TIMS study. Prehnites belong to the oldest vesicular lavas of the *Arqueros Formation* (sample ARQ01-04) and to the oldest vesicular lavas of the *Quebrada Marquesa Formation* (sample ARQ01-01).

Major elements

EDX-SEM analyses (Centro de Instrumentación Científica, Universidad de Granada) permitted the estimation of major element variations. Compositional exchanges are limited to the $\text{Fe}^{3+} \leftrightarrow \text{Al}$ substitution in octahedral sites, expressed as $X\text{Fe}^{3+}$ values ($=\text{Fe}^{3+}/(\text{Fe}^{3+}+\text{Al}^{\text{VI}})$). According to Wheeler *et al.* (2001), only in iron-rich prehnites the $(\text{Fe}^{3+}+\text{Al}^{\text{VI}})$ is larger than 2 *apfu*. In these cases, the excess iron required to fill octahedral sites is taken as Fe^{2+} and added to the seven-coordinated calcium to give $\Sigma^{\text{VII}} = 4.00 \pm 0.01$ *apfu*. Prehnite composition vary widely both within and between individual grains. Prehnite in plagioclase has the lowest $X\text{Fe}^{3+}$ value (0.04-0.03) whereas prehnite in vesicles and fissures have the highest $X\text{Fe}^{3+}$ (0.26-0.41), although when accompanied by calcite in fissures, prehnite shows a lower iron content ($X\text{Fe}^{3+}=0.03$ -0.07).

Trace elements

No data are available on the literature about trace element (including the REE) contents in prehnites. ICP-MS analyses (Centro de Instrumentación Científica, Universidad de Granada) were carried out on hand-picked pure prehnite crystals from vesicles/fissures. Prehnites are characterized by very low Rb content (≈ 0.3 ppm), Sr content ranging from 12.2 to 15.8 ppm, high V values (1077-808 ppm) and extremely variable Ba contents (9.7 to 469.3 ppm).



Differences in the LREE contents exist between the two analysed prehnites, but their Nd, Sm, Eu, Gd, Tb contents and Yb-Lu values are similar (Fig. 2). Different $(\text{La}/\text{Yb})_{\text{N}}$ ratios have been observed between the two analysed prehnites. As compared with their host-rocks, lower REE contents and lower $(\text{La}/\text{Yb})_{\text{N}}$ ratios have been found in the prehnites together with a marked negative Eu anomaly (Fig. 2).

Figure 2.- Chondrite normalized (Nakamura, 1974) pattern of REE in prehnites (filled symbols) and host Lower Cretaceous lavas (open symbols). Data of lava flows from Morata & Aguirre (in press).

Sr isotopes

Sr isotopes were analysed by TIMS (Centro de Instrumentación Científica, Universidad de Granada). Due to the low Rb content, the corrections made of the measured $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio (0.7049-0.7043), based on the Rb and Sr content of prehnite, is almost independent of time. Thus, for an age of 90 Ma the measured present-day $^{87}\text{Sr}/^{86}\text{Sr}$ could be almost considered as the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. In fact, values of $(^{87}\text{Sr}/^{86}\text{Sr})_0$ of 0.7048 (sample ARQ01-04) and 0.7042

(sample ARQ01-01) have been obtained closely in agreement with the measured values. These figures are higher than those of the host lavas (*c.* 0.7036) and also higher than the initial isotopic values of the Late Cretaceous magmatic rocks present in the area (Morata *et al.*, 2003).

DISCUSSION AND CONCLUSIONS

The upper P-T stability for prehnite in metabasites may reach 400°C and up to 3 kb (Liou *et al.*, 1985, Frey *et al.*, 1991) whereas the P-T conditions of the prehnite-pumpellyite paragenesis in the NCMASH system is restricted to the interval 200-280°C and 2-3 kb (Frey *et al.*, 1991). These P-T values are slightly lower than the lowest T values for the hydrogarnet+prehnite paragenesis which, according to Liou *et al.* (1983), for $P \approx 2-3$ kb is *c.* 340°C. Due to the close proximity between the two boundary paragenesis prehnite+pumpellyite and prehnite+hydrogarnet in the sample studied (≈ 200 μm , Fig. 1b) a non-equilibrium crystallisation condition is assumed.

Several studies have shown an influence of T and f_{O_2} in prehnite composition, which becomes more aluminous with decreasing f_{O_2} and increasing temperature (*e.g.* Liou *et al.*, 1983). Low-pressures and temperatures of *c.* 250°C characterise the metamorphic conditions during the Lower Cretaceous in the Coastal Range at the latitude of La Serena. With these P-T constraints, strong variations in the $X_{\text{Fe}^{3+}}$ of prehnites between different grains and within a same grain (see Fig. 1b) must be related to local f_{O_2} variations as a consequence of different fluid/rock ratios or to the effective composition of the paragenetic minerals.

High f_{O_2} conditions during the metamorphism can be deduced based on the strong negative Eu anomaly ($\text{Eu}/\text{Eu}^* = 0.33-0.37$) observed in our prehnites (Fig. 2) which could be interpreted as indicative of the presence of Eu as Eu^{3+} . In these conditions, the Eu must be incompatible in the prehnite and the theoretical substitution of $\text{Ca}^{2+} \leftrightarrow \text{Eu}^{2+}$ is inhibited.

Another thermodynamic control on prehnite composition is related to the a_{CO_2} of the intervening fluids. A very-low a_{CO_2} inhibits the formation of prehnite, even under compatible P-T conditions (≥ 0.01 Parry, 1998 in Wheeler *et al.*, 2001; ≈ 0.002 at $\approx 250^\circ\text{C}$, Digel & Ghent, 1994). Thus, the presence of prehnite and calcite in a same metadomain should be interpreted as been the result of two different events in time. Textural relationships observed in fissures and vesicles indicate that calcite crystallised immediately after prehnite.

The initial Sr isotope ratios in the prehnite can be interpreted as the result of mixing between a magmatic source and meteoric fluids. $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in seawater during the Early Cretaceous (120-90 Ma) was in the range 0.7072-0.7074 (Burke *et al.*, 1982, Mearon *et al.*, 2003). On the other hand, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in limestones intercalated with the lavas of the *Arqueros Formation* give values of 0.7055. The genetic model proposed here to explain the Sr isotopic signature of the prehnites imply fluid-rock interaction processes between fluid convective cells derived from the Early Cretaceous intrusions ($(^{87}\text{Sr}/^{86}\text{Sr})_o \approx 0.7033$, Morata *et al.*, 2003) interacting with the volcanic host-rocks ($(^{87}\text{Sr}/^{86}\text{Sr})_o \approx 0.7036$, Morata & Aguirre., in press) and mixed with Cretaceous seawater.

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