

## <sup>92</sup>Nb-<sup>92</sup>Zr chronometry and early lunar evolution

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<sup>92</sup>Nb decays to <sup>92</sup>Zr with a half-life of 36 Myrs and has the potential to place constraints on the formation and early differentiation of the moon. However, this depends on the initial <sup>92</sup>Nb/<sup>93</sup>Nb of the solar system and the magnitude of early fractionations of Nb from Zr. Assuming that the initial <sup>92</sup>Nb/<sup>93</sup>Nb of the solar system is  $< 3 \times 10^{-5}$  (Schönbächler et al., 2002), <sup>92</sup>Zr isotopic variations are only expected in very old lunar samples and provided Nb is strongly fractionated from Zr. Partitioning studies (Shearer et al., 1996) indicate that ilmenite should have a high Nb/Zr ratio ( $\approx 55$ ). Ilmenite is a common phase in lunar rocks and in addition it has been suggested that high-Ti mare basalts are the product of melting ilmenite-rich cumulate layers formed in the lunar magma ocean (Hubbard and Minear, 1975).

Therefore, we have conducted a comprehensive Zr isotopic study of 9 mare basalts (including 6 high-Ti mare basalts) and two early highland rocks. From the latter (norite 77215 and ferroan anorthosite 60025), we separated feldspar, pyroxene and ilmenite for the determination of internal isochrons. The <sup>92</sup>Zr/<sup>90</sup>Zr can be measured with a precision of  $\pm 30$  ppm (2 $\sigma$ ) on 50 ng Zr using MC ICP-MS. An ICP-DRC-MS was used to determine Nb/Zr without chemical separation (Hattendorf et al., 2001).

The lunar whole rock samples and the mineral separates display no resolvable Zr isotopic variations. The Nb/Zr ratios of the ilmenite fractions of 77215 and 60025 are only 2.3 to 3.3 times higher than chondritic. It has been concluded (Shearer et al., 1996) that the lack of Nb/Zr fractionation in high Ti picritic glasses is inconsistent with assimilation of lunar ilmenite. However, our data show that lunar ilmenites have Nb/Zr ratio much lower than expected. The formation age of 60025 has been estimated at  $4.51 \pm 0.01$  Ga (Hanan and Tilton, 1987) and  $4.44 \pm 0.02$  Ga (Carlson and Lugmair, 1988). Depending on which age is used, the lack of a resolvable <sup>92</sup>Zr anomaly in this rock yields an initial <sup>92</sup>Nb/<sup>93</sup>Nb of the solar system of  $< 1 \times 10^{-4}$  and  $< 5 \times 10^{-4}$  respectively, consistent with our earlier results (Schönbächler et al., 2002).

### References

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## The mechanism of altered layers formation on wollastonite revisited: a combined spectroscopic/kinetic study

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Here we report the results of a study of wollastonite altered layer formation using mixed-flow reactors and various spectroscopic techniques. Dissolution of wollastonite at pH  $< 4$  produced a thick Ca-depleted altered layer as demonstrated by initial more rapid release of Ca relative to Si. After 3000 hours of leaching at pH 1.5-2.2, a completely Ca-free solid is produced. Specific surface area of the powder reacted during 3000 hours at pH 2 increases by a factor of 10000 compared to initial one as measured by B.E.T. N<sub>2</sub> adsorption. Correspondingly, SAXS analyses of powders reacted at the same pH demonstrated, as a function of time, a considerable increase of surface area and internal porosity with preservation of the grains global morphology followed by a grain fragmentation with a consequent reduction of grain size and internal porosity.

Chemical changes of surface layers induced by acid digestion of wollastonite have been investigated by DRIFT and XPS techniques. After 100 hours of reaction, most of characteristic Si-O and Ca-O bands of crystalline wollastonite disappeared and the DRIFT spectra of the solid strongly resembled that of amorphous silica. XPS analysis showed very strong decrease of surface Ca/Si ratio during reaction time of 10-100 h at pH 2 and removal of almost all Ca from the surface after 120 h. XPS also evidences a thinning of the O<sub>1s</sub> peak which reflects the disappearance of non-bridging oxygens. The most important insights on the structure of wollastonite altered layers were gained by using <sup>29</sup>Si MAS NMR spectroscopy. In accord with dissolution rate measurements that suggest the leached layer undergoes reconstructions that produce regions of lower reactivity, polymerization/reorganization of silica tetrahedra with formation of Q<sup>3</sup> and Q<sup>4</sup> structural units at the expense of initial Q<sup>2</sup> was recorded. Quantification as a function of time of the relative proportion of these structural units allowed to correlate the altered layer dissolution rate to its degree of polymerization and to extract rate constants for the different structural units. These results shed new light on the mechanisms of altered layer formation on Ca-silicate surfaces in acid microenvironments like those generated in soils by extracellular products of fungi and bacteria.