

The determination of hydrogen in peridotitic minerals by nuclear methods

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The distribution of H in nominally anhydrous silicates (olivine, pyroxene, garnet) or oxides (ilmenite, rutile, spinel) is poorly known, primarily due to the absence of a suitable analytical technique which has a detection limit in the ppm range. The most sensitive technique used is Fourier-transform infra-red spectroscopy (FTIR), but this involves difficult sample preparation, transparent (in the IR region) minerals and well characterized molar absorbances for different matrices. In addition, it must be assumed that all H present is infra-red active (bonded).

This study describes an alternative technique involving the forward recoil of H from a target by a beam of incident $^4\text{He}^+$ ions (Fig. 1). In this configuration a E- ΔE (tandem) detector system was used and only events recorded in both detectors were accepted as recoils from the target. The Rutherford-backscattered spectrum of He from the target was also accumulated and enabled the accurate determination of beam charge (essential to calculate counts/unit beam charge) for the standardization. The target H-content is then determined by comparison of the counts obtained in an energy spectrum (surface H is excluded from this integration) with standards (Sweeney et al., 1997a). The initial calibration of this method yielded detection limits of ca. 390 ppm H_2O (Sweeney et al., 1997a). However, most recent work using the experimental configuration in Fig. 1 suggests that detection limits of <75 atomic ppm H (ca. 50 wt ppm H_2O) are achievable by this technique (Sweeney et al., 1997b). This is primarily due to the virtual elimination of electronic noise by the tandem-detector system.

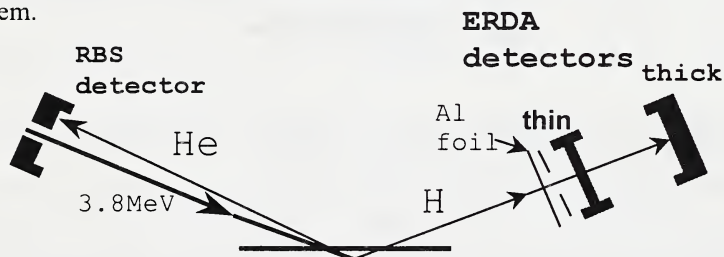


Fig. 1. Schematic representation of the optimal experimental geometry for the determination of H by elastic recoil detection (ERDA or forward recoil) methods. The thin detector is a transmission surface barrier detector and the thick ERDA detector and RBS detector are normal surface barrier detectors (from fig. 1, Sweeney et al., 1997b).

The calibration curve obtained at low-H values using this configuration is shown in Fig. 2. The greatest contribution to the error in precision is the migration of H with time away from the analysis site and the estimate of $\pm 10\%$ relative is based on the multiple analysis of the diopside standard (Fig. 2). Detection limit is estimated based on the analysis of two fragments of natural diamond (D2 and D5) which are used as blanks and it is suggested that the detection limit may be less than the 56ppm H_2O obtained in the lowest-level standard garnet (Fig. 2), a conservative value of 130ppm H_2O is used for the natural material analysed with this calibration.

In addition to the multiple analysis of standard material, a number of measurements were obtained on silicates and oxides from xenoliths in kimberlites from the Kaapvaal and Siberian Cratons (Table 1). It is emphasized that these data are preliminary and more data must still be accumulated using the E- ΔE detector method described above to provide optimal (<130 ppm H_2O) detection limits.

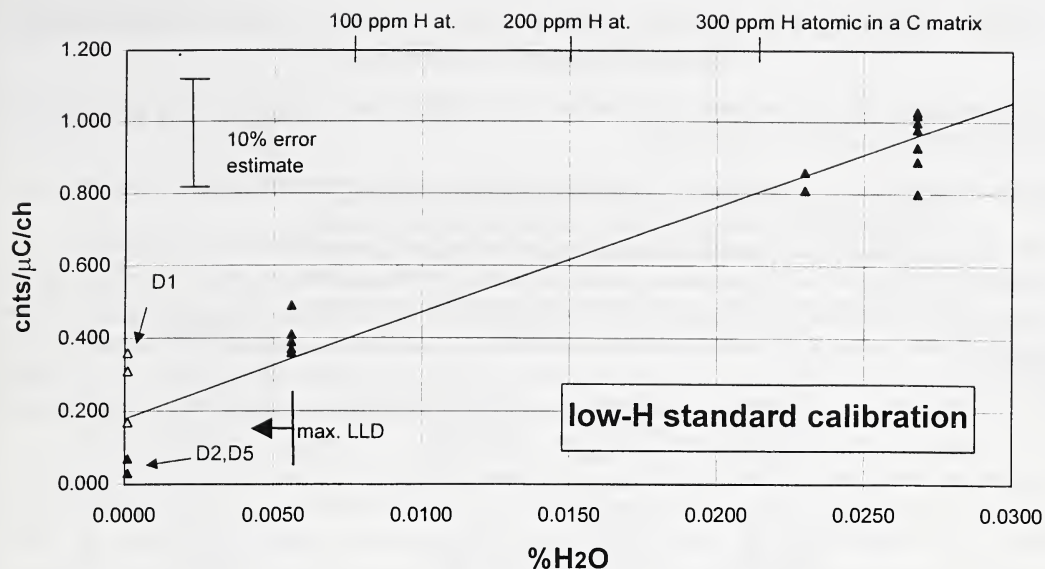


Fig. 2. Empirical calibration of the recoil technique at low-H abundances, constructed for wt% equivalent H_2O and counts/unit beam charge (in μC) integrated over the accumulated channel (energy) range. The standards used are natural garnet (56ppm H_2O), kyanite (230ppm H_2O) and diopside (268ppm H_2O) obtained from G. Rossman (Caltech). The diamonds analysed are plotted on the y-axis and the calibration line is fitted through the solid symbols.

However, although most of these data (Table 1) were obtained with the experimental configuration yielding the higher detection limit (390ppm H_2O), some interesting details emerge. Garnet peridotites from the Kaapvaal (Kimberley, bd20&30) and Siberia (Udachnaya, uda1&2, and Sytyikanskaya, syt2) were analysed. The resolution of any alteration component was problematic: for example the serpentine alteration of a Sytyikanskaya olivine yielded 7.5% H_2O (f87). Although every effort was made to exclude altered areas or cracks from the analysis, it is likely that minerals yielding high H-contents (for example 0.5-1.5wt% H_2O) reflect unseen submicroscopic cracks or alteration. Excluding these high H data ($>0.5\%$ H_2O), pyroxenes from Kimberley contained <390 -3700 ppm H_2O vs <390 ppm H_2O from Sytyikanskaya. The garnets from Kimberley were also more 'hydrous' (<390 -3600 ppm H_2O) than Sytyikanskaya (<600 ppm).

The first analysis of oxide phases yielded 1960-2700 ppm H_2O in three rutiles from a MARID (bd54) and garnet phlogopite peridotite (GPP, bd62) from Kimberley (Table 1). Phlogopites from the GPP sample (bd62) yielded near stoichiometric H_2O contents (4.1-4.5wt%), whereas phlogopites from three MARID xenoliths yielded 3.0-3.6 wt% H_2O (bd54 and Wesselton samples 331&422). These low H_2O contents are not imposed by chemical effects due to (for example) excess F; F is $0.23 \pm 0.1\%$ in MARID phlogopites (Konzett, 1996). It is suggested that the low K/H ratio in the MARID phlogopites reflect the ratio in the melt or fluid from which the phlogopite crystallized: the abundance of K (and the nature of the bulk composition) ensured high modal phlogopite, but insufficient H_2O was available to accommodate the stoichiometric requirements of this volume of phlogopite. It is likely therefore that the MARID assemblage crystallized from a H_2O -undersaturated melt rather than a hydrous K-bearing fluid. In contrast, phlogopite in peridotite most likely crystallized from a fluid or melt with a lower K/H ratio.

The elastic recoil technique affords an opportunity to accumulate data to a detection limit of ca. 50ppm H_2O (H-equivalent) on polished sections, including opaque minerals. Surface adsorbed H_2O is easily resolved (and excluded) in this technique. The technique employs beam sizes of 5-

15µm, making studies on the spatial distribution of H within minerals possible. The technique is not species-specific as bulk H is determined.

Table 1. Hydrogen (in pm) in peridotitic minerals, determined from empirical calibrations of H-bearing standards (Sweeney et al., 1997a). Analysis numbers are in brackets for analyses using different standardizations: m-series with a higher detection limit of 1000ppm H2O and f-series with detection limits in the range 130-390 ppm H2O. Precisions in the ppm range are +-10% relative and in the % range +-5% relative.						
	ol	opx	cpx	ga	duplicates:	
Kaapvaal						
GP						
bd20	880 (f194)	3700(f99)	1290 (f97)	<390 (f119,120, 121)	(119-121)	
		1.10%(f192)	900 (f185)	3630 (f187)	(187-189)	
		0.76%(f193)	1070 (f186)	2811 (f188)	(190,191).	
		1.35% (f190)	1150 (f189)	(192,193).		
		1.51% (f191)				
bd30		450 (f52)	<390 (f51)	<390 (f55)	(51,54,58)	
		640 (f53)	649 (f54)	<390 (f56)	(55,56)	
		1680 (f561)	1.13% (f58)	<390 (f62)	(59,60)	
		1.56% (f59crack)				
		<390 (f60)				
Siberian GP (Hz)						
uda1	<390 (f65)	<390 (f68)		470 (f64)	(67,69)	
	<390 (f66)			<390 (f67)		
				<390 (f69)		
synt2	510 (f85)		<390 (f89)	610 (f83)	(83,84)	
	570 (f86)			540 (f84)		
	7.5%(f87alt)			510 (f88)		
				<390 (f90)	(90,91)	
			<390 (f91)			
uda2 (hz)	560 (f95)				(95-97)	
	<390 (f96)					
	<390 (f97)					
	<390 (f98)					
	150 (f231)					
	<130 (f232)					
	200 (f233)					
	ga	cpx	kricht	phg	rutile	ilmenite
MARID						
bd54		<390 (f10)		3.6% (f12)	1960 (f13)	
		620 (f11)				
331				3.0% (m70)		
422			2.0% (m84)	3.4% (m83)		
GPP						
bd62				4.5% (m86)	2680 (m88)	
				4.1% (m98)	2150 (m93)	
				4.1% (m99)		
PKP						
XM1-356						1380 (m116)
Eclogite						
Rovic1	605 (f92)	1050 (f94, inclusion in f92/93)				
	<390 (f93)	<390 (f95)				
		<390 (f96)				

References:

- Konzett, J. (1996), PhD thesis, ETH-Zurich, pp295.
 Sweeney et al. (1997a). *Geochimica Cosmochemica Acta*, 61, p. 101-113.
 Sweeney et al. (1997b). *Nuclear Instruments and Methods B*, in press.